The Effect of Nickel to Zinc Ratio in Nickel-Zinc-Ferrites Nanoparticles on Its Magnetisation for Application in Enhanced Oil Recovery

By

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A Project Dissertation submitted in partial fulfilment of

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CERTIFICATION OF APPROVAL

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…………………………….
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TRONOH, PERAK

May 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own expect as specified in the references and acknowledges, and that the original work contained herein have not been undertaken or done unspecified sources or persons.

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(Muhamad Erwani bin Aziz)

ABSTRACT

The inability of natural drive mechanism of the reservoir to produce oil to the surface is the major problem faced by the oil and gas industry today. This research is mainly focusing on the method to recover the remaining oil after secondary recovery which is the Enhanced Oil Recovery (EOR) method. EOR method is essential in oil and gas industry nowadays since the natural drive mechanism can no longer bring up oil to the surface after time of production increases. In this study, the influence of magnetic nanoparticles on the oil recovery efficiency is being observed. The magnetic nanoparticles that are being used is Nickel-Zinc-Ferrites. The main objectives is to synthesis Nickel-Zinc-Ferrite magnetic nanoparticles into five different ratios of Nickel to Zinc by using Sol-Gel method. Then, the nanoparticles will be characterized using Thermal Gravimetric Analysis (TGA)**,** X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Vibrating Sample Magnometer (VSM). The sample of X=0.5 shows highest magnetization which is 61.9 emu/g out of five samples which is annealed at $900^{O}C$. The samples that annealed at $900\ ^{O}C$ shows better magnetic saturation compared to the samples annealed at $700^{O}C$. Later, the nanofluid will be prepared using the deionised water as the dispersing fluid to be injected into the core sample in the core flooding experiment. This core flooding experiment will measure the oil recovery efficiency by evaluating the produced oil from the core sample after the secondary recovery stage. The sample X=0.5 shows highest oil recovery which is about 16% from Residual Oil in Place (ROIP). Thus, the highest magnetization among the five samples of the magnetic nanoparticles which will affect the oil recovery was determined and the objective was achieved.

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CONTENTS

List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

1.1 Background

Today, the technology of enhanced oil recovery (EOR) has been developed in order to extract the remaining oil in the reservoir after the primary and secondary recovery. The third recovery or EOR is a technique that can recover about 30%-40% of remaining oil in the reservoir [1] thus can increase the revenue for the oil and gas company. To recover the oil after the first and second recovery, various conventional oil recovery techniques has been introduced and used. For instance, the injection of gases such as CO_2 is injected in the reservoir by compressor to achieve miscibility in order to move the oil to the production zone [2]. Besides, there are also chemical injection such as surfactant and polymer to increase the mobility of the oil by decreasing the interfacial tension between oil and water.

The high temperature and high pressure in the reservoir creates difficulties to recover the oil using the conventional oil recovery methods. For example, the chemical or gas injection to recover the oil cannot be applied at the high temperature and high pressure condition as the injection agents start to change the properties under the condition [3]. The more the depth, the higher the temperature and pressure thus it will be more difficult and creates more challenges to bring the oil to the surface.

The development of nanoparticles has been a new phenomenon where recent research have shown that the nanoparticles can alter a certain factor in the oil properties and formations thus can bring such a huge benefit for oil recovery. Binshang has reported that reservoir that have water wet formation produce better than oil wet formation. These nanoparticles can change the wetting phase in the reservoir hence helps in EOR recovery [4].

In recent studies, magnetic nanoparticles have shown positive results in oil recovery efficiency. The nickel-zinc-ferrite is being used as an oil recovery efficiency agent. The Nickel-Zinc-Ferrite is being used because it has shown the following properties such as low eddy current, high resistivity and high saturation magnetization [5] that helps in the oil recovery efficiency.

1.2 Problem Statement

Nowadays, the oil and gas industry are having a challenging problem in recover the remaining oil in the well to fulfil the hydrocarbon demand in around the world. The production of crude oil is decreasing because there is not enough pressure to bring the crude oil to the surface even the natural drive of the oil production cannot helps in produce the oil in large quantity. As this problem occur, many oil companies had involved with research to help increase the production by using different techniques in Enhanced Oil Recovery (EOR) method. In recent years, many different types of magnetic nanoparticles have been used and tested in EOR technique for instance Zinc Oxide, Ferro fluid, Zirconium Oxide, Tin oxide and Silicon Oxide [6].

The oil in the reservoir after the primary and secondary recovery usually have high interfacial tension and high viscosity to move in the porous media. Due to high pressure also, this remaining oil in the reservoir, basically around 30%-40% balance need to be extracted in order to achieve the economic value. Based on one of the research that study the effect on magnetisation on drilling fluid, the recovery of oil is higher with injection of optimized drilling fluid to achieve higher recovery [7].

This research will study on the effect of the magnetisation of the nanoparticles, Nickel-Zinc-Ferrite on the recovery. The Nickel-Zinc-Ferrite with various composition of Nickel and Zinc exhibit different properties such as thermal, electrical, chemical properties and magnetisation; the most important parameter in this research [7]. The composition of the Nickel-Zinc-Ferrite are synthesized with the Sol-Gel method with different composition ratio of nickel and zinc to have a different magnetisation effect. Then, the Nickel-Zinc-Ferrite will be tested in core-flooding experiment to see the efficiency of different ratio of nickel to zinc in recovery of oil.

1.3 Objectives and Scope of Study

1.3.1 Objectives

1) To synthesis the nickel-zinc-ferrite nanoparticles at five different ratio of Nickel to Zinc using the Sol-Gel method.

2) To determine the magnetisation of five samples of Nickel-Zinc-Ferrite nanoparticles

3) To study the effect of magnetisation of the nanoparticles on the oil recovery efficiency using core flooding experiment.

1.3.2 Scope of Study

In this study, the magnetisation effect on the recovery of residual oil in the reservoir will be validated. This research will focus on Nickel-Zinc-Ferrite where this nanoparticles will be synthesized using the Sol-Gel method. The general formula for Nickel-Zinc-Ferrite is $Ni_{1-x} Zn_x Fe_2 O_4$. Through this experiment, five samples will be produced with the changing value of x which are x=0, x=0.25, x=0.50 and x=0.75 and x=1. So, the samples will have different magnetisation that will be measured using the Vibrating Sample Magnetometer (VSM) Testing.

In order to investigate the structure of nickel-zinc-ferrite, the samples will be characterized using the x-ray diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM) technique. The XRD will determine the structural phase of the prepared sample [8] while the FESEM will establish the crystallography of the nanoparticles such as crystallite phase, size and structure [9].

Then the sample will be tested using Vibrating Sample Magnetometer (VSM) to measure the magnetisation of the five samples to determine the magnetisation of different ratio of Nickel to Zinc is achieved. All the data of XRD, FESEM and VSM testing will be recorded prior to the result of the research to see whether the magnetisation will have effect to the nanoparticles in recovery of the oil in the reservoir. To validate the objective of this research to recover more oil, core flooding experiment will be conducted to test whether the magnetisation of Nickel to Zinc ratio has effect or not on the recovery efficiency. In the core flooding experiment, the samples will be dispersed in the ionised water as the base fluid (solvent) to form the nanofluid. Then the nanofluid will be injected into the compacted glass bead (core sample) and the amount of oil recovered from the core will be evaluated

CHAPTER 2

LITERATURE REVIEW

2.1 Enhanced Oil Recovery (EOR)

Enhanced Oil Recovery (EOR) has been a newest technology in recovery the oil in the reservoir. In Indonesia oil production had decreased from 1.434 million barrels per day in 1995 to 1 million barrels per day in 2007 which about 15% decline from year to year [10]. But, with EOR, the declination had been reduced to 6.7% per year hence increase back the profit. EOR is the methods used to improve the oil extraction by injecting different kind of materials which can change the physics and chemical properties of fluid in the reservoir rocks.

There are three types of oil production recovery to get the maximum product in oil exploration and production (E&P).

i. **Primary Recovery** = Production of oil only use the natural power to bring the oil to the surface for instance natural water movement, gas expansion and changes in pressure.
ii. **Secondary Recovery** = Introduce the gas or water injection for oil recovery to push the oil from the rock as natural drives is decreasing. The basic concept is to maintain the pressure of the reservoir as the primary recovery
iii. **Tertiary Recovery** = Extracting oil left behind after the primary and secondary recovery that also known as enhanced oil recovery and generally use more effective fluids as recovery agent.

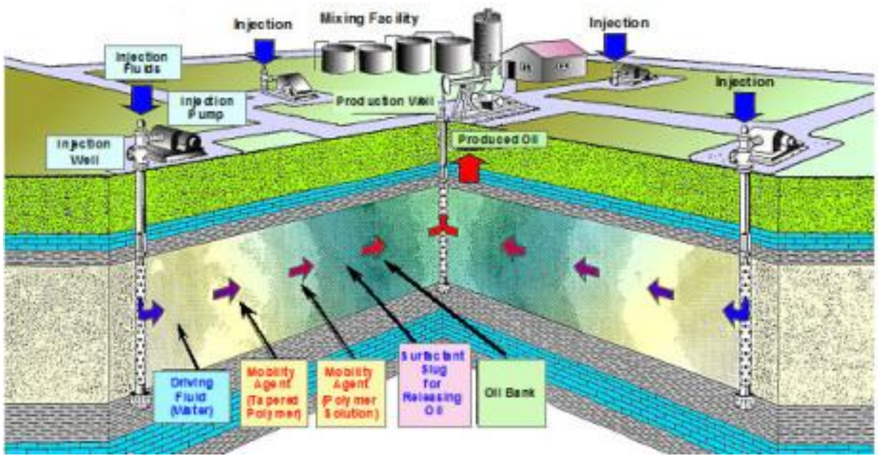

Figure 2.1: EOR process in field [2]

The availability of oil is because of the reservoir rock's heterogeneity. Only a part of the reservoir which can be swept by the fluid pressure whereas about 10%-40% unwashed oil remained stuck after secondary recovery in the pore volume due to high capillary pressure (Pc) and also interfacial tension (IFT) [11]. Besides, the large viscosity of the last oil also can hinder the flow rate to be extracted economically. So the usage of nanoparticles that being injected with the drilling fluids help to recover the last oil thus can produce the remaining balance oil in the reservoir. The study based on the magnetisation effect of the nanoparticles will help to increase the percentage of oil recovery.

2.2 Nanoparticles in Enhance Oil Recovery (EOR)

Nanoparticles had known to be a good recovery agents for problems occur in reservoir especially to recover the remaining oil in the production zone after first and second recovery. There are two reasons why the nanoparticles particularly attractive to be developed and research in the oil and gas business which are firstly is the size of the nanoparticles that have one dimension in the order of 100 nm or less and secondly the ability to manipulate the behaviour [12]. The spherically shaped of nanoparticles will be injected and transported successfully through the formation rock without any nanoparticles are trapped due to chemical, physical straining or electrostatic effects with the surface charge that compatible in the porous media [13].

There are some selected types of nanoparticles that are likely used for research and studies for instance Aluminium, Zinc, Magnesium, Iron, Zirconium, Nickel, Tin, Ferrite and Silicon [6]. It is essential to study the effect of different nanoparticles in oil recovery since this is the main objective of the oil and gas industry. In this research the author will use the Nickel-Zinc-Ferrite nanoparticles that are synthesized at different composition ratio of Nickel to Zinc. The Nickel-Zinc-Ferrite has found used in electromagnetic applications that require a high permeability such as inductors and electromagnetic wave absorbers [7]. The ability of the nanoparticles that can change a few factor of oil properties and in the formation [7] by introducing the nanoparticles and studying the effect on oil recovery efficiency.

In order to use nanoparticles as an EOR agents, some parameters need to be determined to ensure the efficiency of nanoparticles. In Hendraningrat et al research, they study about the effect of some parameters that influencing the oil recovery process such as nanoparticles size, rock permeability, injection rate and temperature. The hydrophilic silica nanoparticles had been chosen to be used in the experiment. This study shows that the oil that can be recovered in the core samples with the smallest size of nanoparticles because of the contact angle between the oil and rock has been decreased thus facilitate the displacement process [14]. Nanoparticles sizes play an important role in the efficiency in Enhanced Oil Recovery (EOR).

Besides, the Hendraningrat et al also said, temperature also gives some effect on oil recovery using the nanoparticles. He said that, the increasing temperature may increase the oil recovery efficiency [14]. This had been explained by focusing on the interaction between the molecules which are weaker thus decreasing the Interfacial Tension (IFT). By decreasing the IFT, the mobility ratio of oil is increased and make the movement of oil to the production zone easier [11]. All the experiment temperature in the experiment is keep constant to ensure the changing temperature may affect the result.

Nanoparticles existed in solid state after synthesized. In order to measure the oil recovery efficiency, the nanoparticles is dispersed in dispersing fluids and become nanofluids. One of the example of nanofluids is ferrofluid which are found to be partially magnetically controllable and smart nano-material [15]. The ferrofluid contains three elements which are the magnetic particles, surfactant and also liquid carrier [15]. The addition of the surfactant in the ferrofluid is to cease agglomeration which means the surfactant will prevent the nanoparticles from clumping together. The liquid carrier is as the solvent or the based fluid for instance deionise water, ethanol, diesel and brine [6]. Ogolo et al report that, the deionised water may become the best dispersing fluid or solvent for certain nanoparticles such as ferrites and oxides [6]. The nanofluids that form with distilled water has decrease the recovery efficiency. Ogolo et al stated that the distilled water may emphasized the significant role a fluids play because it can contribute positively or negatively in oil recovery [6].

Ferrofluid is a mixture of magnetic nanoparticles which is Nickel-Zinc-Ferrites nanoparticles in a carrier fluid or base fluid usually water or oil. When subjected to a magnetic field, the apparent viscosity of the ferrofluid will increase and it is known as viscoelastic [15]. Once the apparent viscosity is increased, it can push up the oil to the production zone to be extracted to the surface. According to Kothari, the viscosity of the magnetic fluid is depend on two factor. First is the viscosity of the carrier fluid (base fluid). Second, it is depend on the applied magnetic field when the core-flooding experiment is conducted. [15]

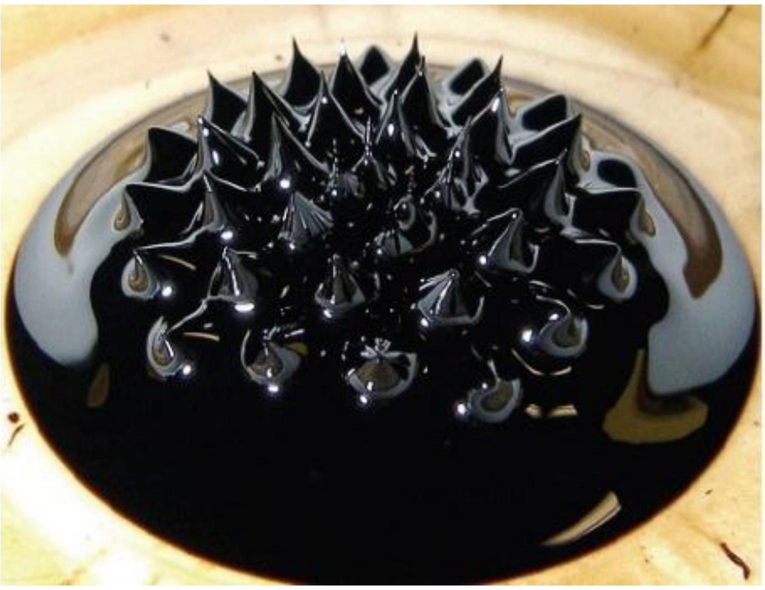

Figure 2.2: Ferrofluid under magnetic effect [15]

For this research, the Nickel-Zinc-Ferrite will be dispersed in the deionise water to form the nanofluids. This nanofluids will be injected into the core sample to measure the oil recovery efficiency by the nanoparticles. Hendraningrat et al conclude that, the injection rate of the nanoparticles that are being injected into the core sample need to be constant. The increasing injection rate eventually will decreasing the oil recovery as the nanoparticles may accumulate at the core inlet rather than flowing into the core [14].

Yahya (2012) said in his experiment, the recovery factor percentage with nanofluids injection without EM wave is about 8.7% while the recovery factor percentage of nanofluids with EM wave increase the percentage up to 13.6% [12]. This shown the effectiveness of the nanofluids is more when exposed under electromagnetic wave.

CHAPTER 3

METHODOLOGY

3.1 Flow Chart

The figure below summarize the workflow and also experimental design for this research.

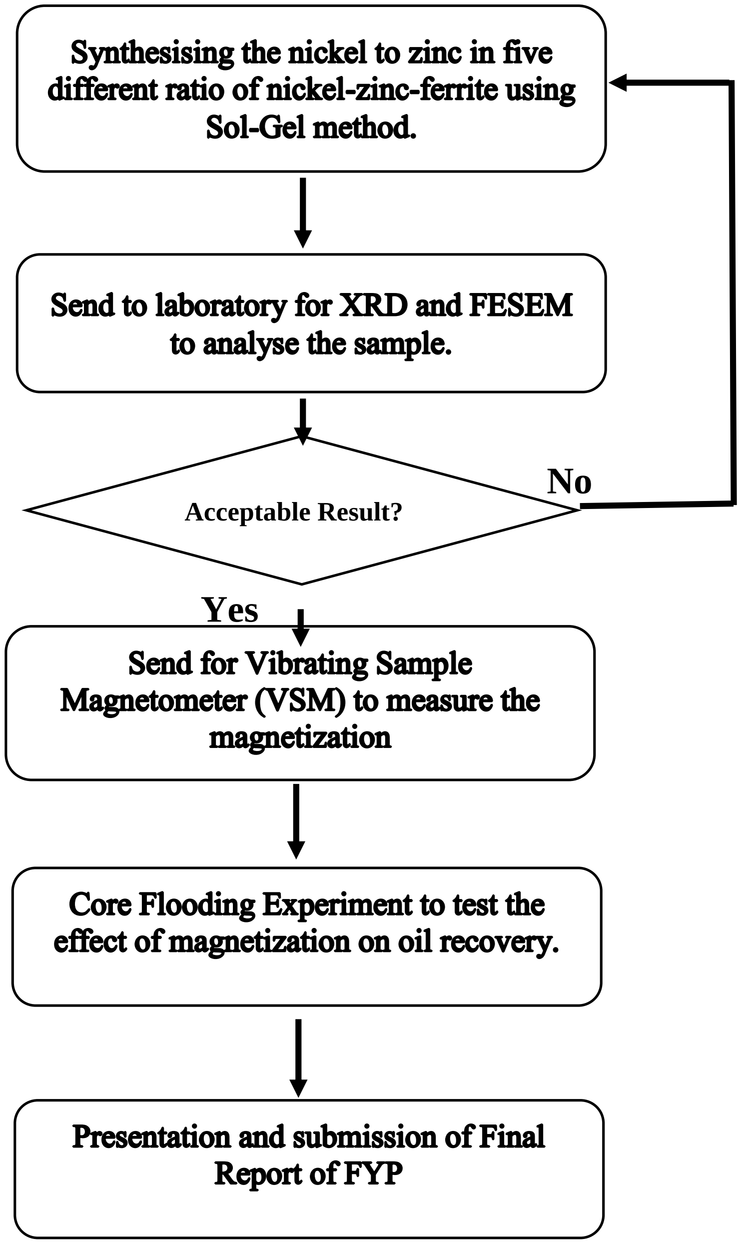

Figure 3.1: The flowchart process

3.2 Synthesized the Nickel-Zinc-Ferrites.

There are various techniques that have been used to synthesis the nanoparticles for instance sol-gel, hydrothermal and thermal evaporation [15]. In this research, sol-gel method have been chosen as the technique. It is because due to its simplicity means easy to conduct the synthesising process, low cost and the ability to control its properties and structure by changing different parameters such as type of solvent, annealing temperature, stirring period, precursor material and others. [5]

The table 3.1 show the composition ratio of the three elements in Nickel-Zinc-Ferrite:

Table 3.1: composition ratio of nickel and zinc

Samples	**Nickel**	**Zinc**	**Ferrite**
1	1%	0%	Constant
2	0.75%	0.25%	Constant
3	0.5%	0.5%	Constant
4	0.25%	0.75%	Constant
5	0%	1%	Constant

By using the Sol-Gel method, the starting materials that are used to start with are as follows:

I. $Ni(NO_3)_2 \cdot 6H_2O$ – Nickel (II) Nitrate

II. $Zn(NO_3)_2 \cdot 6H_2O$- Zinc (II) Nitrate

III. $Fe(NO_3)_3 \cdot 9H_2O$ – Iron (III) Nitrate

The three starting materials with different weight samples were dissolved in the 100ml citric acid that have been prepared. Then the solutions was stirred using the magnetic stirrer with a constant rate about 200rpm at room temperature. The sample was left stirred for about 2-3 hours to mix all the materials. Then, the sample was heated on the hot plate at 80^{o}C and be kept heated until the stirring bar was stopped and the gel was formed. Next, the gel was heated in the drying oven at temperature about 110^{o}C for two days until it dried. Then, the dried gel was collected and crushed into powder.

Then, the powder was annealed at two different temperature which is 700˚C and 900˚C, which is the optimum temperature to form powder with nanosizes.

There are five samples with different ratio composition of Nickel and Zinc in the Nickel Zinc Ferrites. The table 3.2 show the formula of the produced samples. The general formula is $Ni_{1-x} Zn_x Fe_2 O_4$.

Table 3.2: Chemical formula of Nickel-Zinc-Ferrite samples

No of Samples	*Samples Formula*
1, x=0	$Ni_1 Fe_2 O_4$
2, x=0.25	$Ni_{0.75} Zn_{0.25} Fe_2 O_4$
3, x=0.5	$Ni_{0.5} Zn_{0.5} Fe_2 O_4$
4, x= 0.75	$Ni_{0.25} Zn_{0.75} Fe_2 O_4$
5, x=1	$Zn_1 Fe_2 O_4$

All the calculation is shown in the appendix.

3.3 Particle characterization

3.3.1 X-Ray Diffraction (XRD)

XRD is a technique like a fingerprint of a substance. The XRD technique is basically suited for identification and characterization of the crystalline phases. A crystal structure is being built by layers or planes. The X-rays with a wavelength which is same to the distances between this planes can be reflected. The angle of the reflection is known as angle of incidence and this behaviour likely to be called as diffraction. Besides, the peak intensities will gives information about how much the X-ray is contributing to the reflection for instance how much phase is present in a sample.

Diffraction pattern analysis will help to determine the phases in a sample. So, it is possible to determine and quantify each phase present, the crystallinity of the sample, the lattice parameters, the crystal structure and all others material characterization for a sample. Figure 3.2 shows the XRD equipment.

Figure 3.2: The XRD equipment

3.3.2 Field Emission Scanning Electron Microscope (FESEM)

FESEM equipment is shown in the figure 3.3 to capture the grain image of the nanoparticle. The field emission microscope consists of the metallic sample in the tip and a conducting fluorescent screen which is enclosed in an ultrahigh vacuum. The electron that are generated by the field emission source is accelerated in a field gradient. The beam that passes the electromagnetic lenses will focus on the sample. The sample will produced a secondary electron which will be captured by the detector and the image of the sample will be generated.

Figure 3.3: The FESEM equipment

3.3.3 Vibrating Sample Magnometer (VSM)

The VSM is an instrument that is used to measure the magnetization of these samples. The samples will be magnetized by putting the sample inside a uniform magnetic field. The sample will be vibrated sinusoidally. The lock-in amplifier will measure the induced voltage using the piezoelectric signal as the reference. By measuring the external electromagnet field, the hysteresis curve can be formed. Hysteresis curve is when an external magnetic field is applied to a ferro magnet such as iron; the atomic dipoles align themselves with it. Once the magnet had been magnetized, it will stay it that form. Heat or magnetic field in opposite direction is needed to demagnetize the magnet.

3.3.4 Core Flooding Experiment

The core flooding experiment is basically an injection of fluids into the core sample to see the recovery efficiency of the fluids to displace the existing fluids in the core. The core flooding experiment is performed in an ambient temperature condition. The sequences of the fluid injection is brine, crude oil, brine and lastly the nanoparticles which being prepare in liquid form known as nanofluid. This experiment is the ways to stimulate the real process in the reservoir to enhance oil recovery. The figure 3.4 show the setup of the experiment.

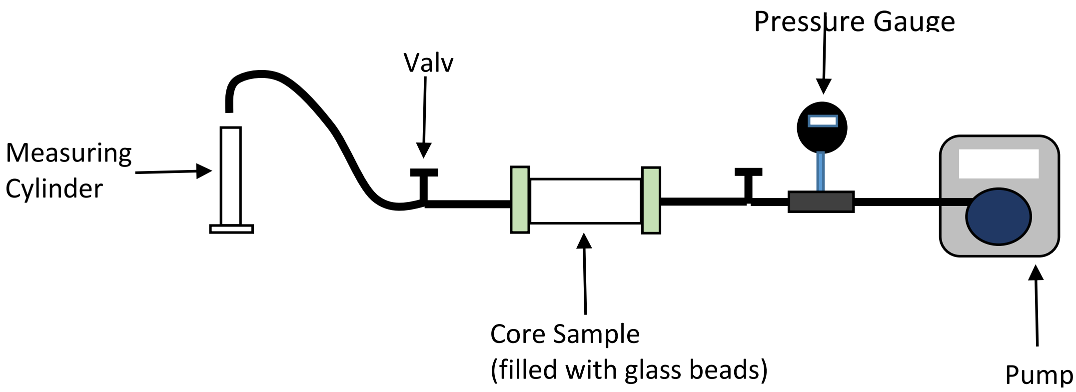

Figure 3.4: The core-flooding setup equipment

Firstly, brine was injected in the porous media (core sample) which wasfilled with the two different sizes of glass bead. At this stage the pore volume is calculated using the formula:

$$pore\ volume = \frac{weight\ difference\ (g)}{Density\ of\ the\ brine\ (\frac{g}{mL})}$$

Noted that the weight difference in the formula indicates the weight difference between the weight of wet core sample and weight of dry core sample.

After the brine had fully saturated the core, then the crude oil was injected into the core. The brine produced at the measuring cylinder will be collected and measured. The oil would push the brine out of the pore in the core. The volume of the brine collected is equal to the volume of the oil in the core which is known as the Original Oil in Place (OOIP). Then, the brine will be injected again into the core to simulate the secondary recovery until no more oil is produced.

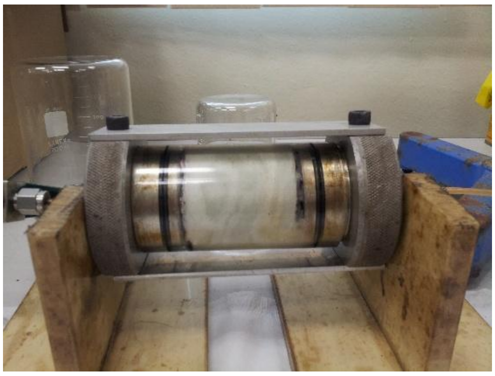

Figure 3.5: The brine being injected into the core sample and slowly saturated the core at rate 1mL/min

Figure 3.6: The crude oil being injected into the core sample and slowly saturated the core at rate 0.8 mL/min

The nanofluids were prepared to simulate the tertiary recovery. The Nickel-Zinc-Ferrite nanoparticles was dispersed into the deionize water to form nanofluids. The nanoparticles was ultrasonicated for about one hour to make sure the nanoparticles was dispersed well in the deionize water. The concentration of the nanofluids will be kept constant throughout the experiment which is about 0.1 wt %.

The crude oil recovered by the nanofluid was collected as effluent using the measuring cylinder. As the crude oil was produced, the nanofluid was also is produced and was collected in the measuring cylinder. In order to take the reading, the collected fluid was left for at least 15 minutes to differentiate between the crude oil and the nanofluid or brine. This phenomenon is due to different density between the crude oil and also the nanofluid or brine. The figure 3.7 shows the collected fluid after the nanofluid injection.

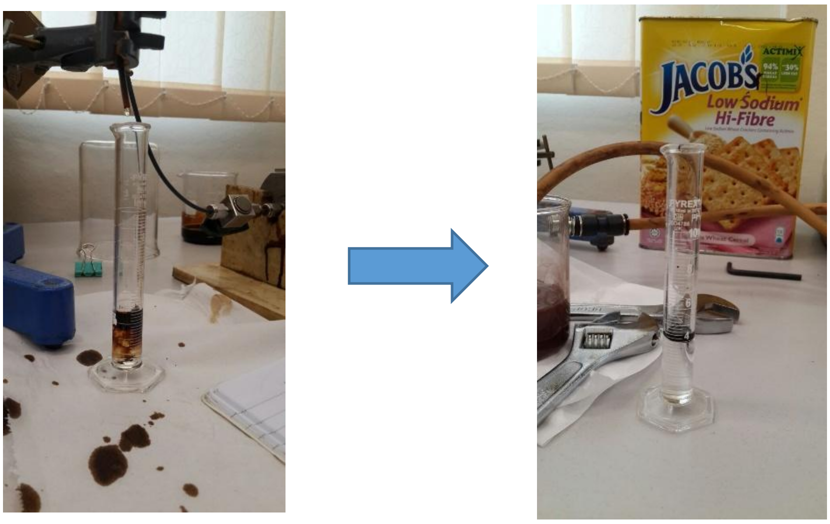

Figure 3.7: The crude oil + nanofluid collected

The figure below shows the collected crude oil that being recovered during the tertiary recovery injection.

Figure 3.8: The crude oil that has been recovered

3.4 Gantt chart

FYP 1

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Topic collection														
2	Preliminary research, discuss with SV, RO and collect data														
3	Synthesising three sample														
4	Submission Extended Proposal														
5	Proposal Defence														
6	sample characterization (XRD, VSM)														
7	Draft submission of Interim Report														
8	Submission of Interim Report														

Figure 3.9: The Gantt chart of FYP 1

FYP 2

No	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Sample characterisation (XRD,VSM)															
2	Nanofluid preparation															
3	Recovery Test (core flooding)															
4	Submission of Progress Report															
5	Pre-SEDEX															
6	Submission of Draft Final Report															
7	Submission of Dissertation (softcopy)															
8	Submission of Technical Paper															
	Viva															
10	Submission of Dissertation (hardcopy)															

Figure 3.10: The Gantt chart of FYP 2

Process

Key milestone

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results

All five samples have been synthesized using the Sol-Gel method consists of different ratio of Nickel to Zinc which are 1:0, 3:1, 1:1, 1:3 and 0:1. The table below shows the chemical formula for the five nanoparticles samples. The general formula for Nickel-Zinc-Ferrite nanoparticle is $Ni_{1-x}\,Zn_x\,Fe_2\,O_4$.

Table 4.1: The chemical formula of the five samples

Samples	*Samples Formula*
x=0	$Ni_1\,Fe_2\,O_4$
x=0.25	$Ni_{0.75}\,Zn_{0.25}\,Fe_2\,O_4$
x=0.5	$Ni_{0.5}\,Zn_{0.5}\,Fe_2\,O_4$
x= 0.75	$Ni_{0.25}\,Zn_{0.75}\,Fe_2\,O_4$
x=1	$Zn_1\,Fe_2\,O_4$

The figure 9 below shows some of the Nickel-Zinc-Ferrites nanoparticles that are already synthesized.

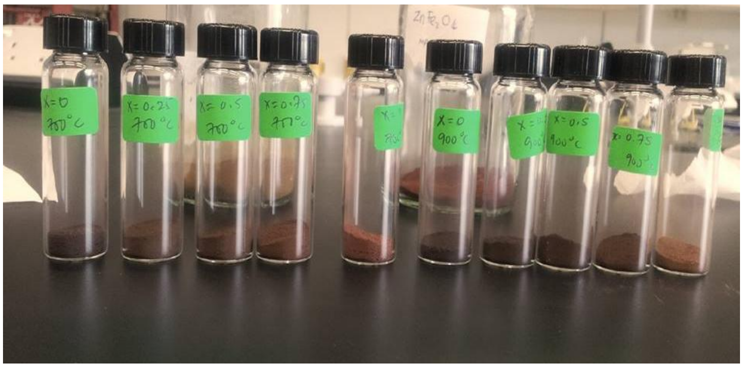

Figure 4.1: The Nanoparticles samples.

4.1.1 Thermal Gravimetric Analysis (TGA) Results

All of the five samples are tested using the TGA analysis to identify the best temperature for calcination process. The figure below show the result of the TGA

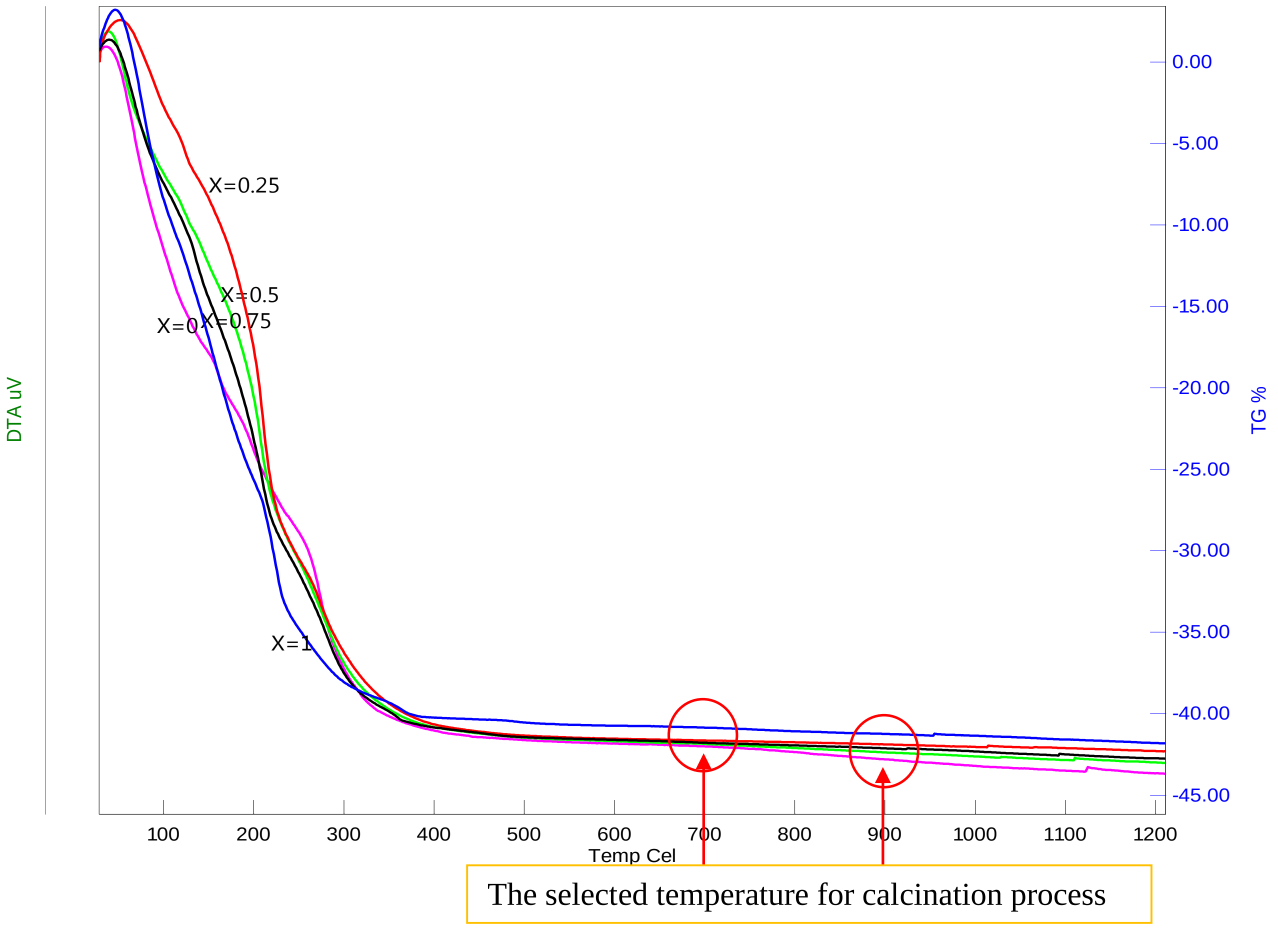

Figure 4.2: The TGA Graph Result

The optimum temperature for calcination process is based on the graph when it is become constant which means that no more weight loss due to decomposition and loss of water, combustion evaporation and vaporization. The temperature of the calcination is selected at $700^{\circ}C$ and $900^{\circ}C$ by looking at the constant phase of all the five samples. Both of the temperature are selected as annealing temperature to see the relationship between magnetization effect and also temperature. This relationship is obtained using the VSM Testing.

4.1.2 X-ray Diffraction (XRD) Results

For the XRD results, the characterization of the ten samples are determined. The figure 4.3 show the example of the Nickel Zinc Ferrite standard card that indicates the formation of pure cubic structure in the annealing temperature.

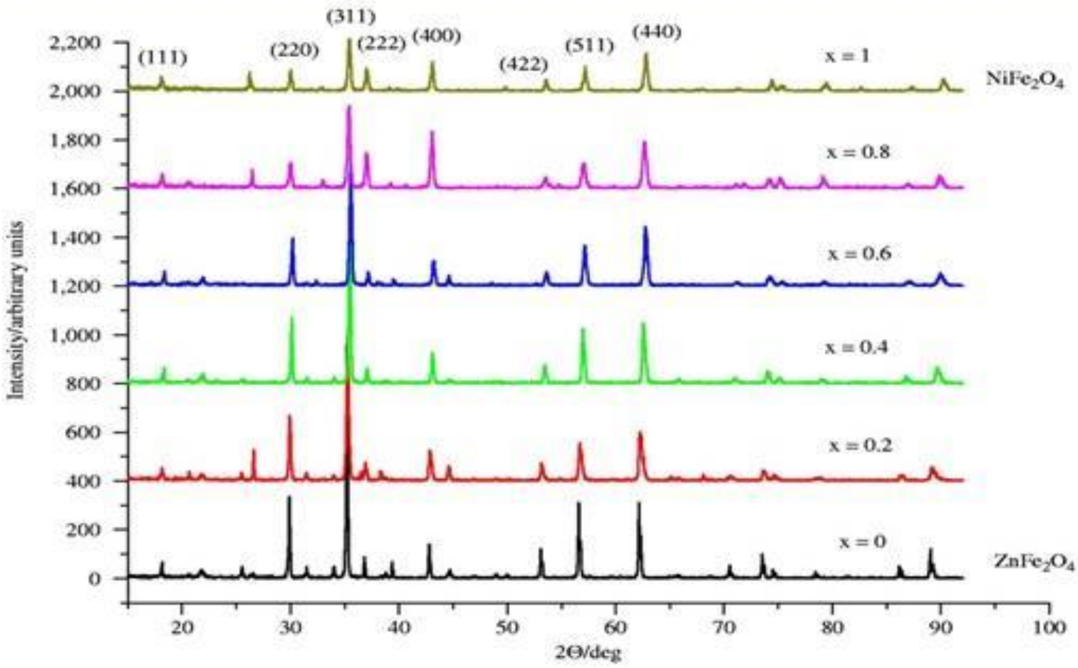

Figure 4.3: The standard card of Nickel-Zinc-Ferrites Nanoparticles

It is very important to compare the peak of the XRD results with the standard card to make sure that the samples actually are Nickel Zinc Ferrite without other impurities exists in the samples. If there are others impurities contain, it may affect the cubic spinal structure as well as affect the magnetization.

From the graph also, the average crystallite size of the nanoparticles of various composition of Nickel and Zinc element can be calculated using the Scherer's equation.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where:
K =0.9 θ = Bragg's Angle
B = FWHM λ = X-ray wavelength (1.5406 Åm)

The table 4.2 and table 4.3 shows the crystallite size that were calculated using the formula. All the data was analysed in the XRD software. Based on the calculation, sample X=0.5 shows the highest crystallite size for both annealing temperature. This result can be validate using the FESEM result to see the difference in crystallite and particles size.

Table 4.2: Crystallite size for 700˚C Temperature

Calcination Temperature = 700˚C			
Samples	2-Theta	FWHM	Crystallite size (nm)
x=0	47.33	0.8039	11.27
x=0.25	42.85	0.2886	30.9
x=0.5	43.70	0.2755	32.46
x=0.75	42.62	0.3280	27.16
x=1	51.36	0.3436	26.8

Table 4.3: Crystallite size for 900˚C Temperature

Calcination Temperature = 900˚C			
Samples	2-Theta	FWHM	Crystallite size (nm)
X=0	47.60	0.2854	31.79
x=0.25	41.00	0.2165	41.00
x=0.5	107.90	0.1181	119.36
x=0.75	42.54	0.1246	71.49
x=1	42.64	0.1509	59.05

The figures 4.4 to figure 4.8 shows all the results of XRD Testing for the samples annealed at $700^{O}C$.

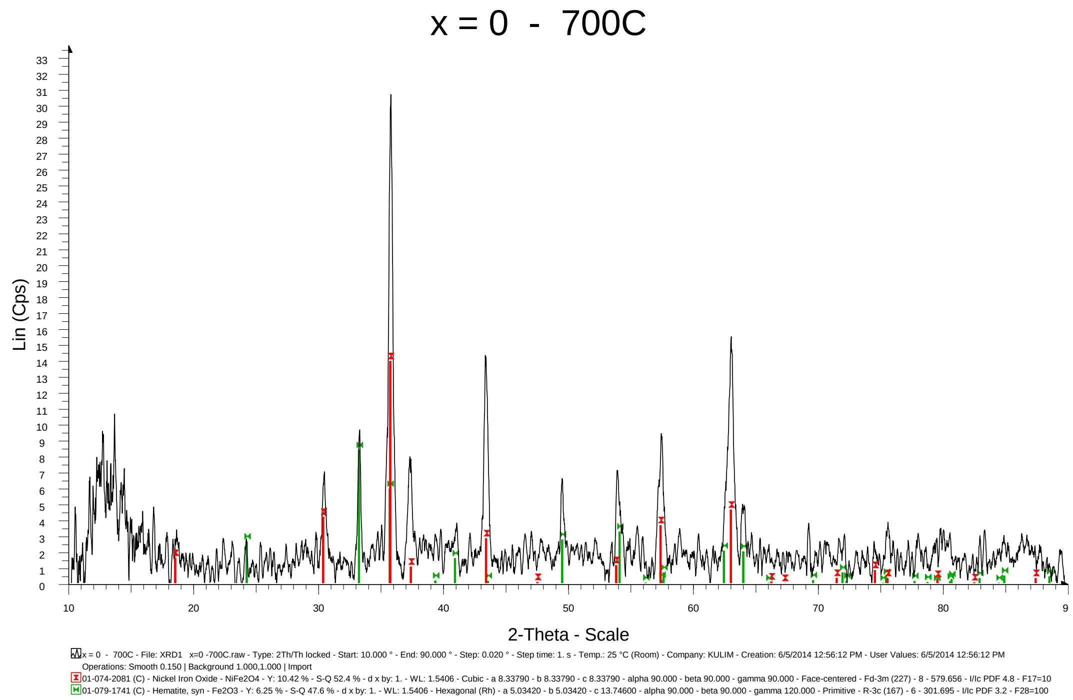

Figure 4.4: Result XRD for X=0 at $700^{O}C$

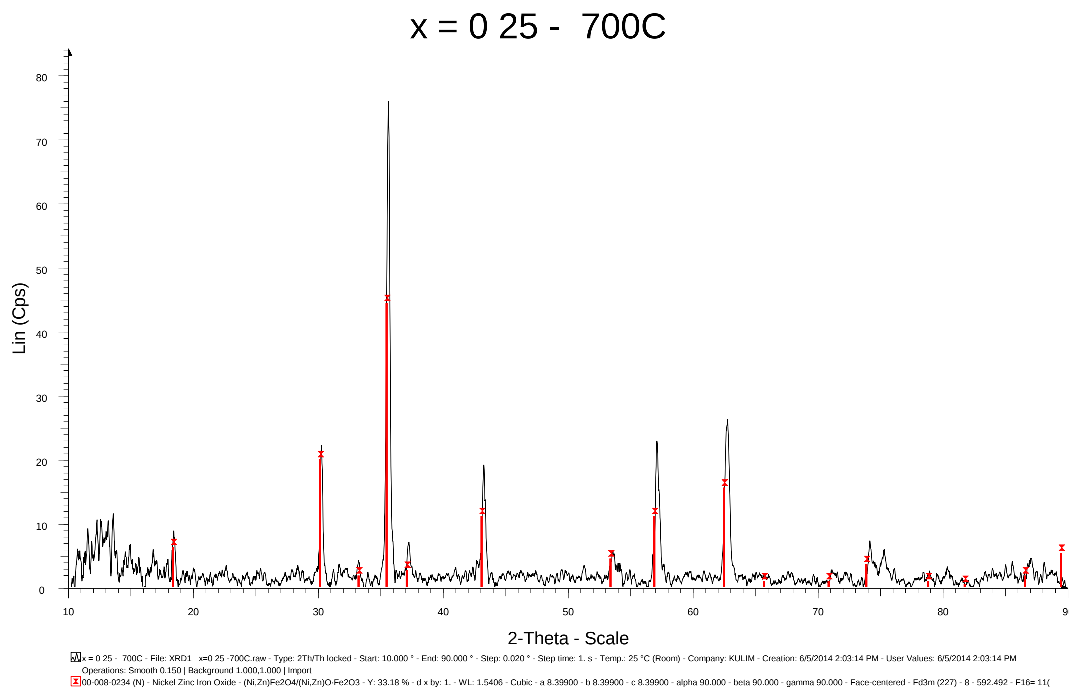

Figure 4.5: Result XRD for X=0.25 at $700^{\circ}C$

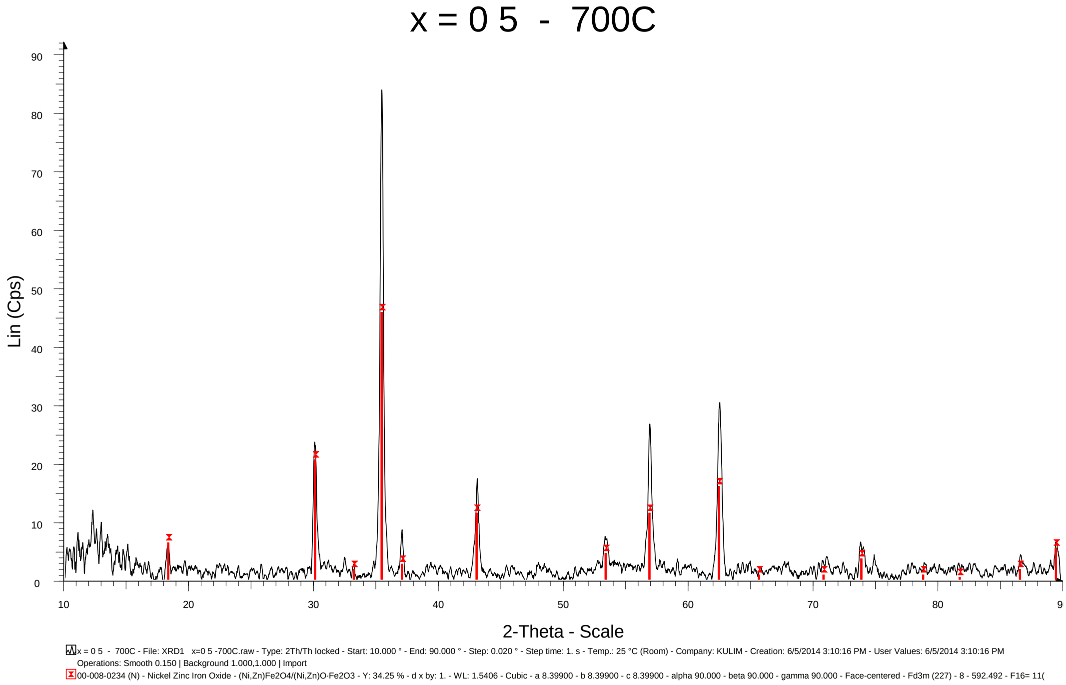

Figure 4.6: Result XRD for X=0.5 at 700˚C

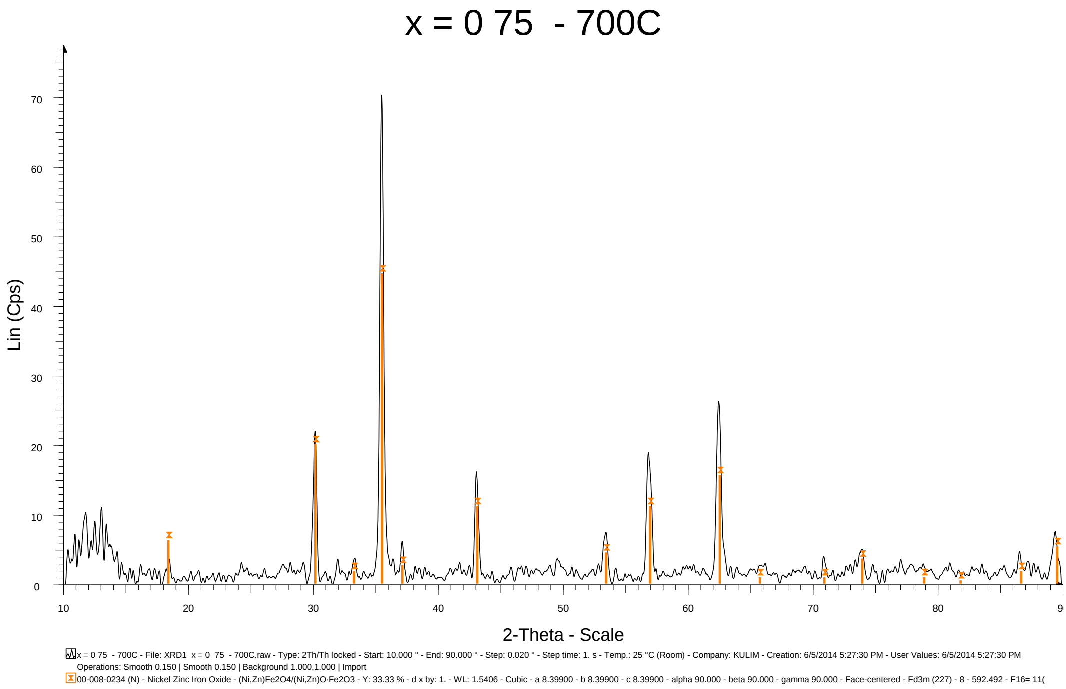

Figure 4.7: Result XRD for X=0.75 at 700˚C

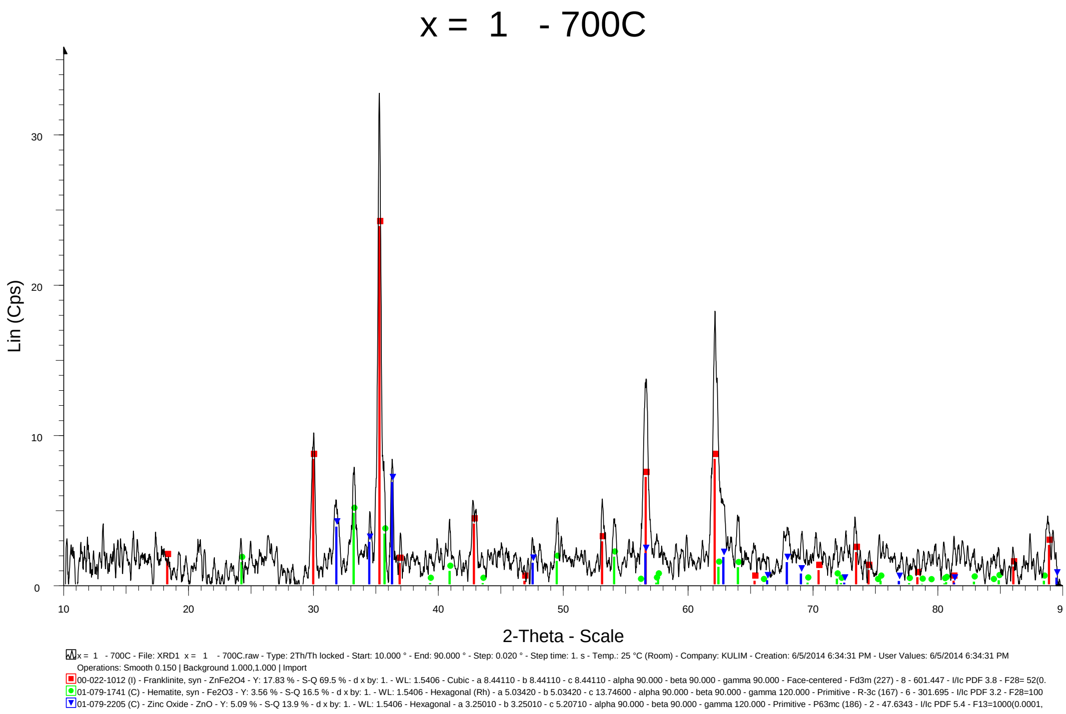

Figure 4.8: Result XRD for X=1 at 700^{O}C

The figure 4.9 show the summary of the XRD result which at 700°C of annealing temperature.

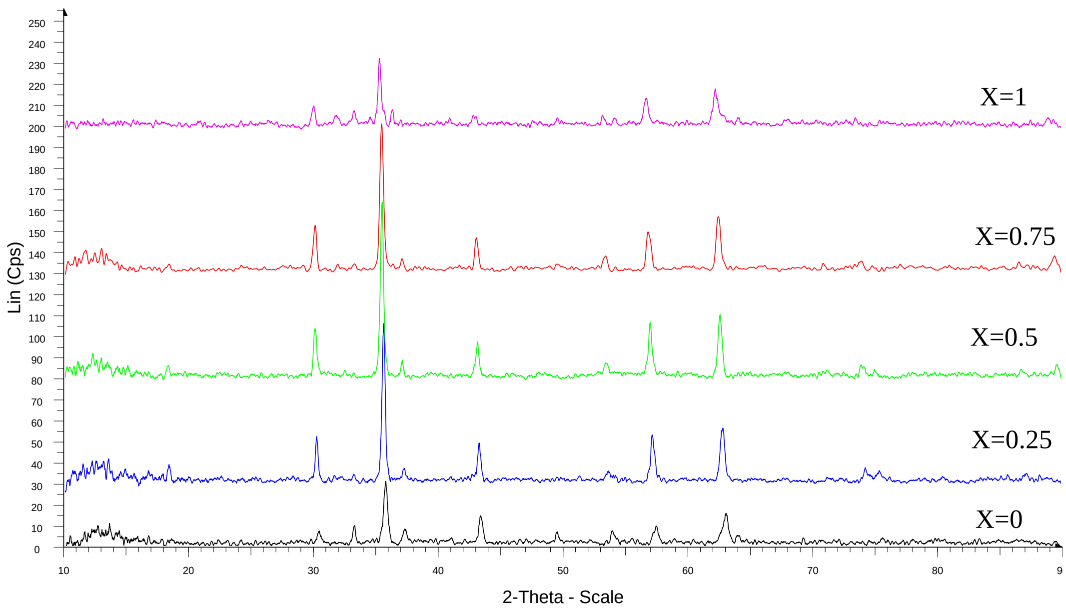

Figure 4.9: Summary Result XRD at 700°C

The figures 4.10 to figure 4.14 shows all the results of XRD Testing for the samples annealed at 900°C

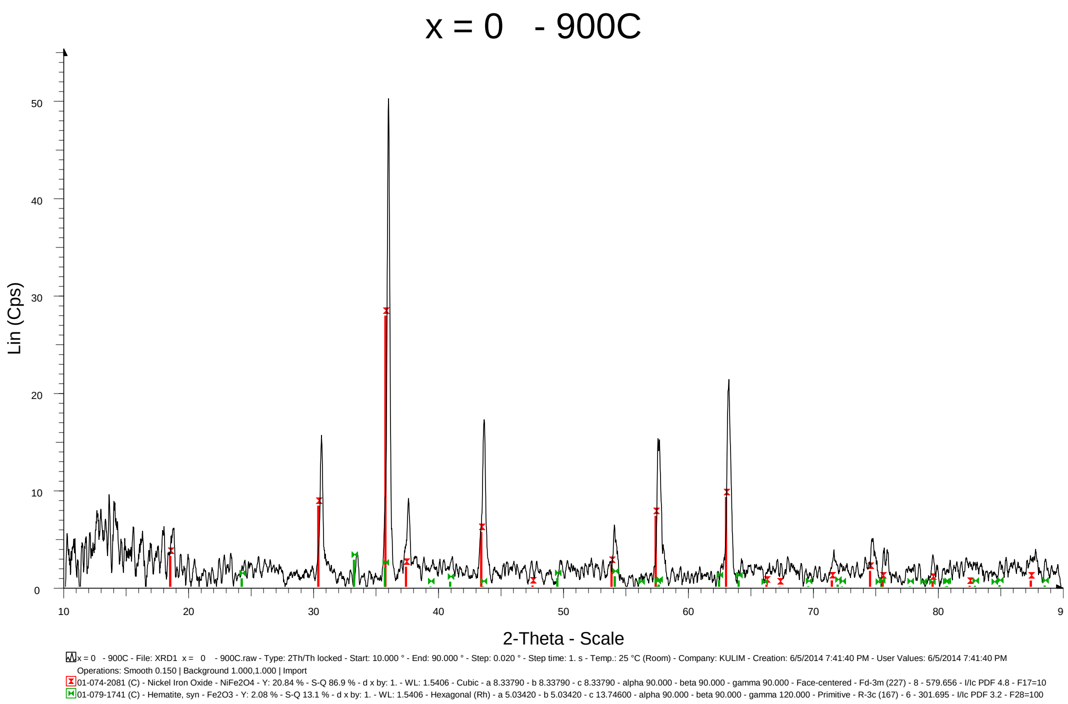

Figure 4.10 : Result XRD for X=0 at 900°C

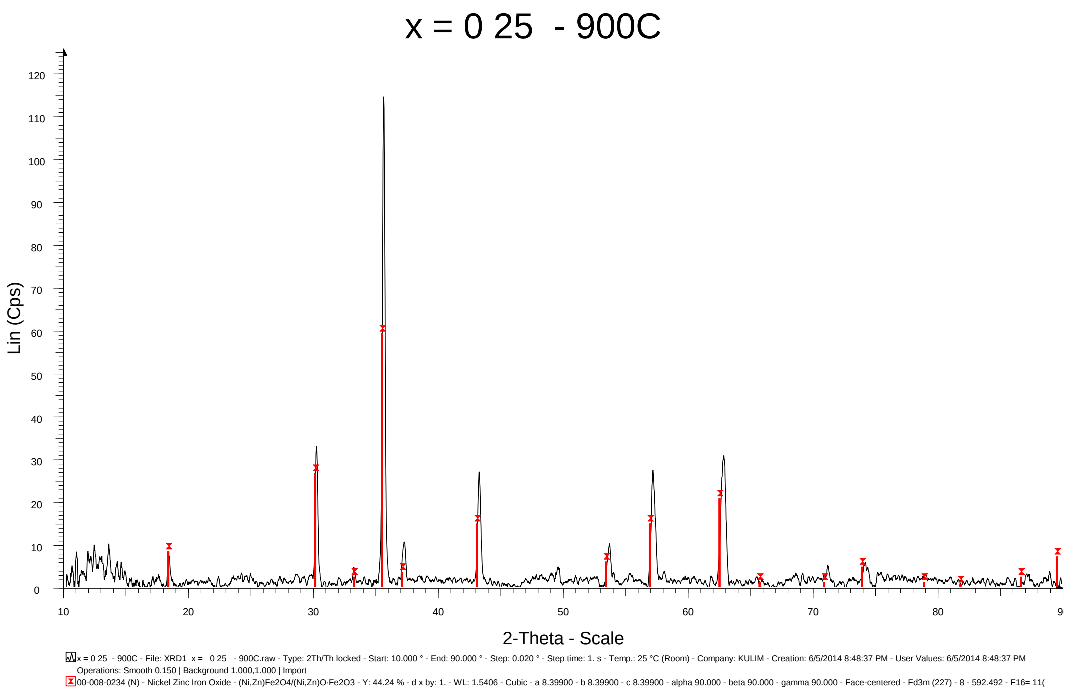

Figure 4.11: Result XRD for X=0.25 at 900°C

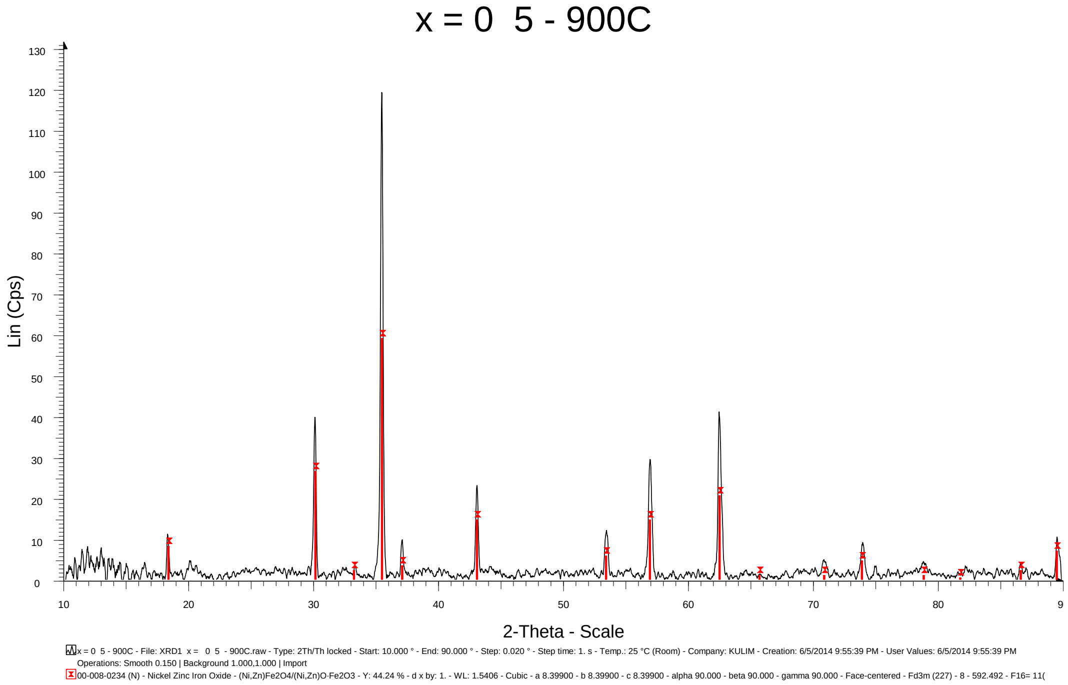

Figure 4.12: Result XRD for X=0.5 at 900°C

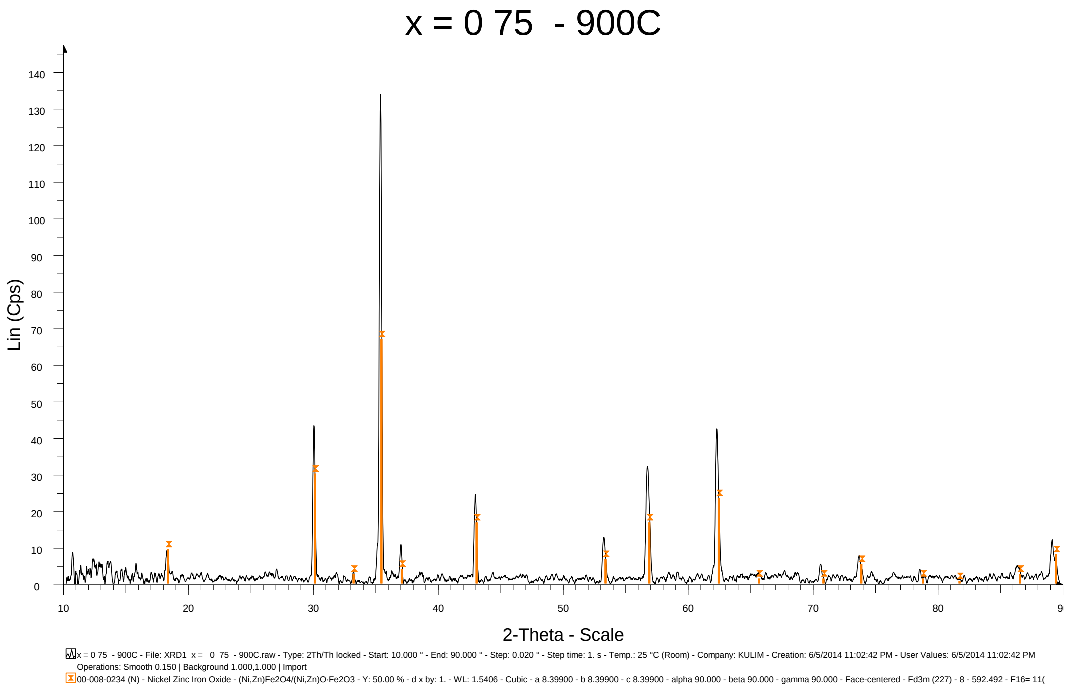

Figure 4.13: Result XRD for X=0.75 at 900°C

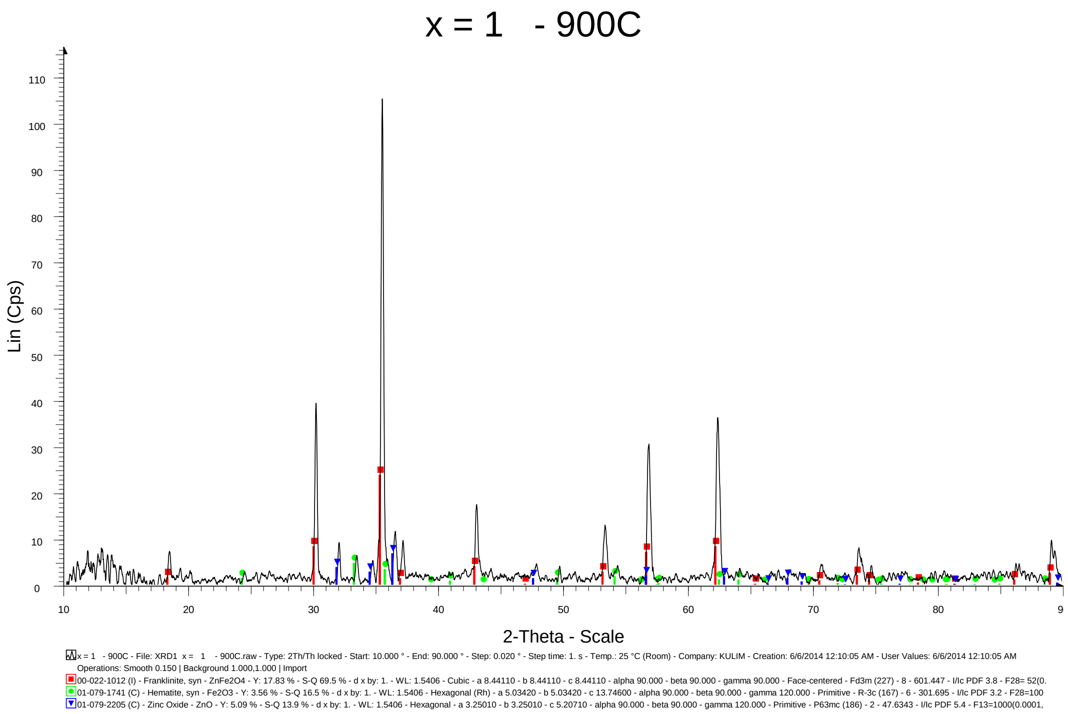

Figure 4.14: Result XRD for X=1 at 900°C

The figure 4.15 show the summary of the XRD result which at 900^{O}C of annealing temperature.

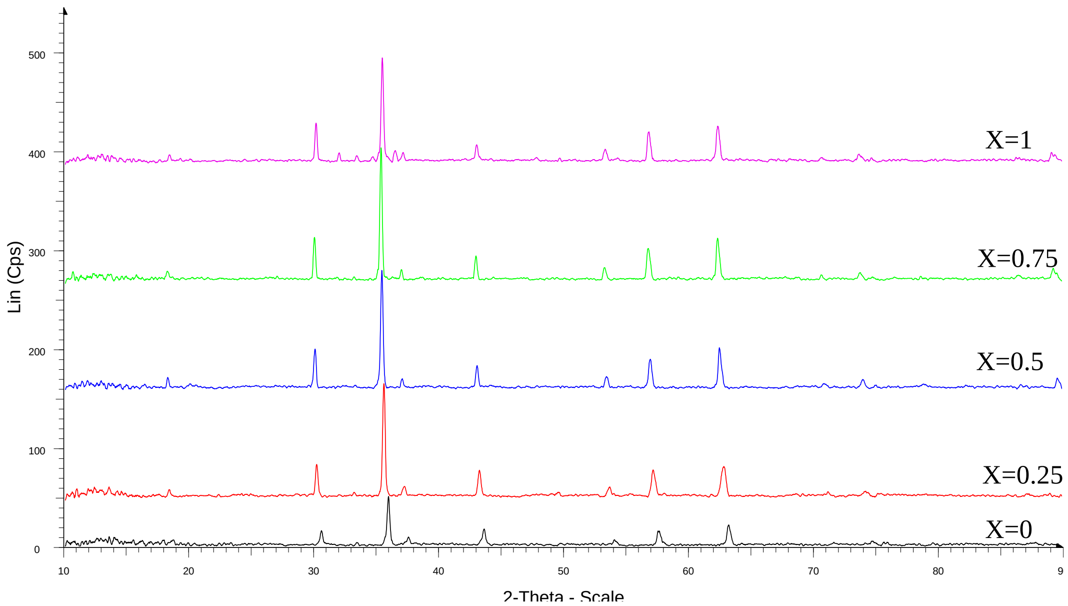

Figure 4.15: Summary Result of XRD at 900°C

4.1.3 Vibrating Sample Magnetometer (VSM) Results

The magnetization saturation is determined using the testing. Below are the results of all the VSM Testing for ten samples.

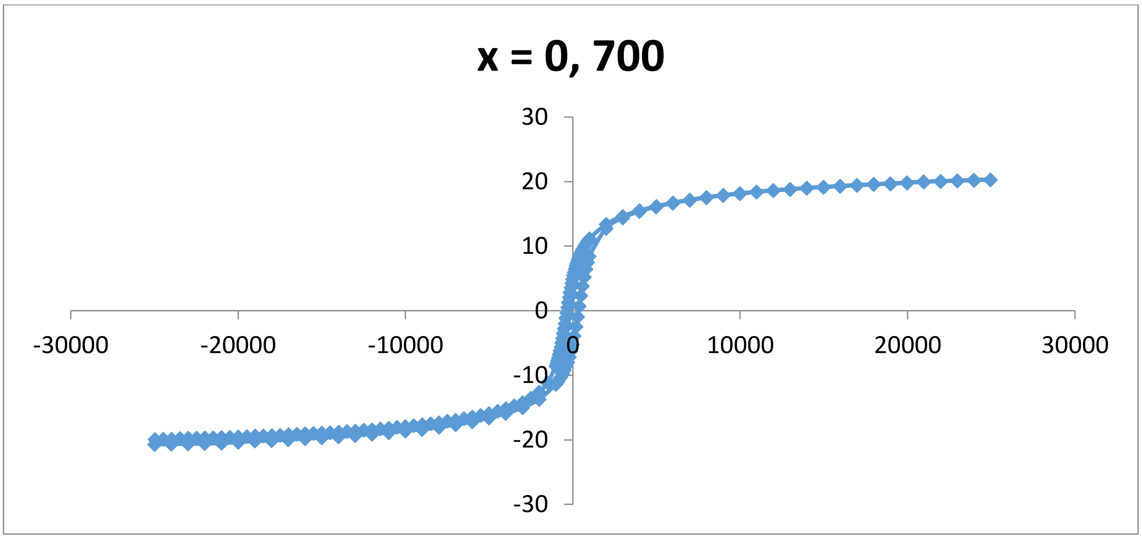

Figure 4.16: Result VSM for X=0 at 700°C

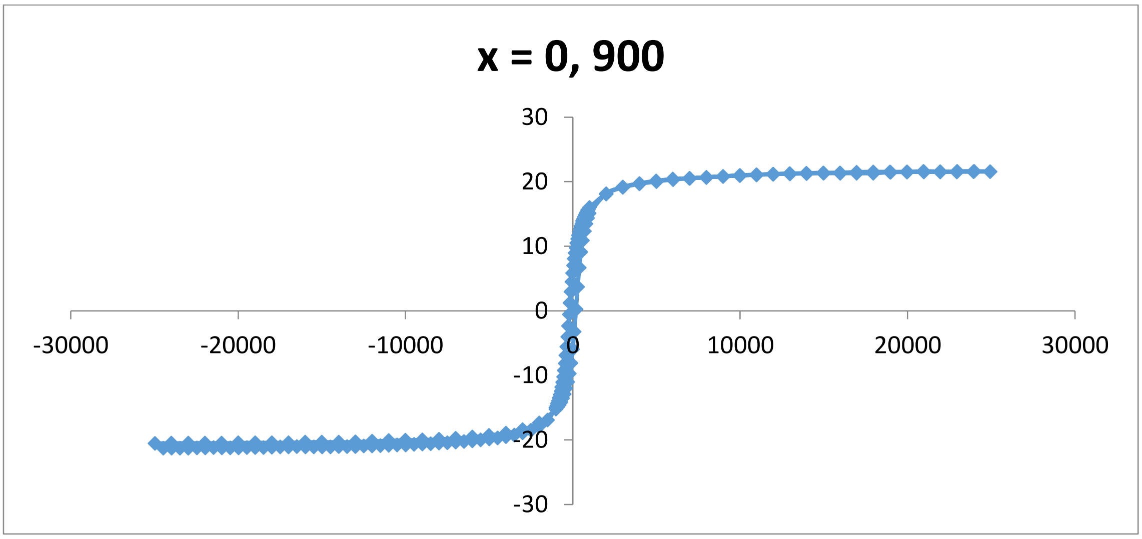

Figure 4.17: Result VSM for X=0 at 900°C

The figure 4.16 and figure 4.17 shows the magnetic saturation of the sample, $Ni_1 Fe_2 O_4$ (X=0) of two different temperature which are 700°C and 900°C.

Temperature (°C)	Magnetic Saturation (emu/g)
700	20.3
900	21.6

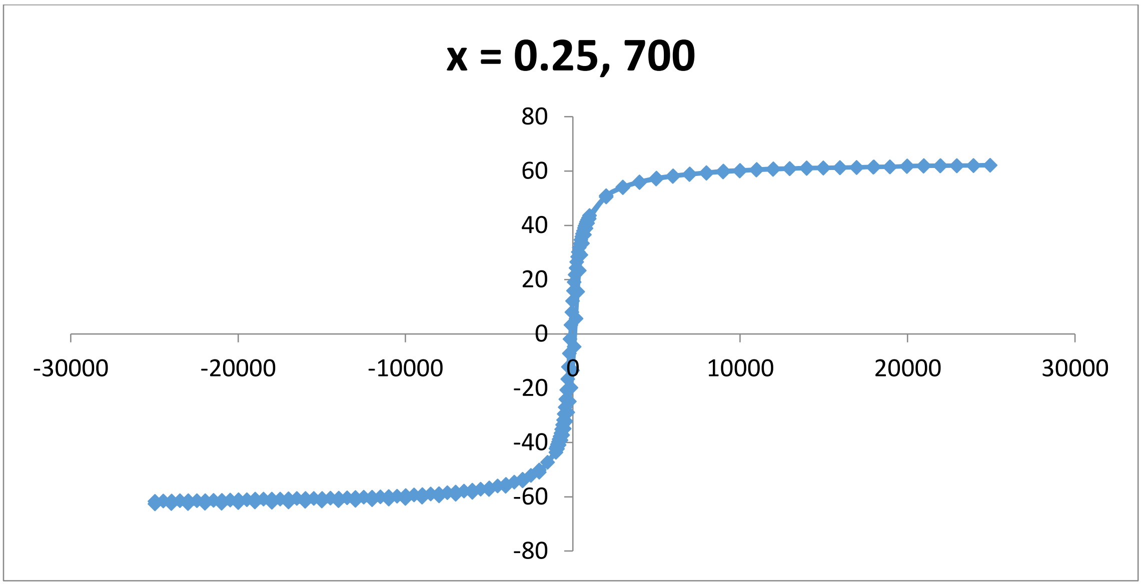

Figure 4.18: Result VSM for X=0.25 at 700°C

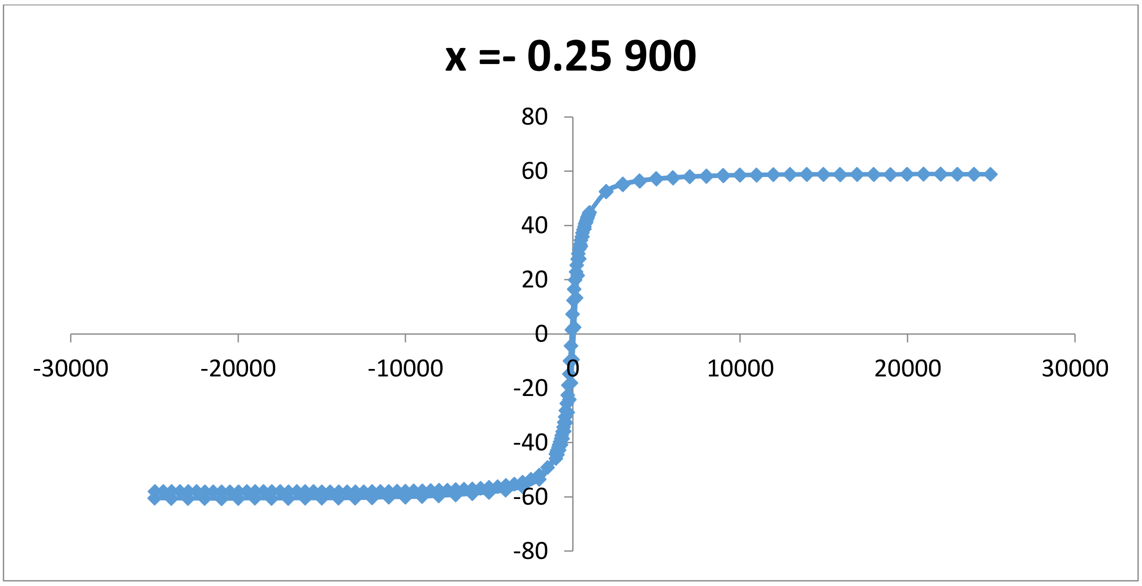

Figure 4.19: Result VSM for X=0.25 at 900°C

The figure 4.18 and figure 4.19 shows the magnetic saturation of the sample, $Ni_{0.75}Zn_{0.25}Fe_2O_4$ (X=0.25) of two different temperature which are 700°C and 900°C.

Temperature (°C)	Magnetic Saturation (emu/g)
700	58.9
900	59.2

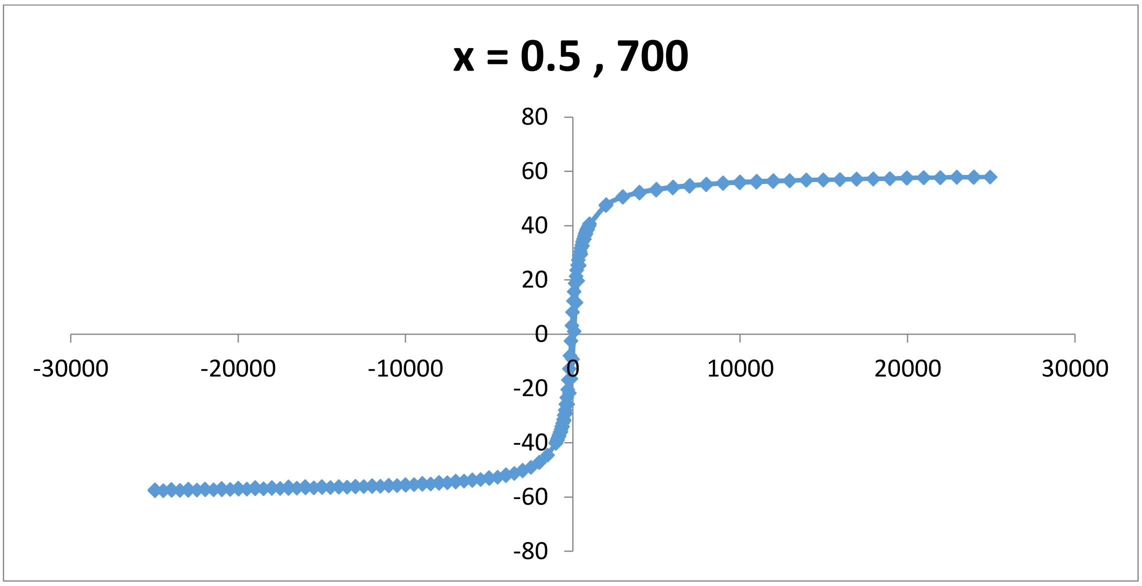

Figure 4.20: Result VSM for X=0.5 at 700°C

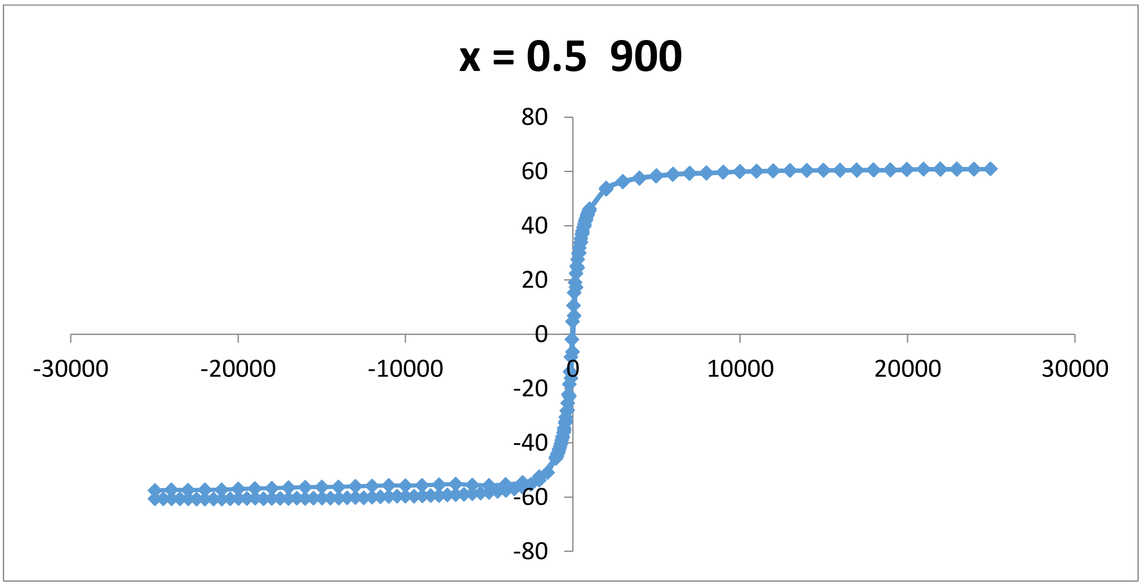

Figure 4.21: Result VSM for X=0.5 at 900°C

The figure 4.20 and figure 4.21 shows the magnetic saturation of the sample, $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (X=0.5) of two different temperature which are 700°C and 900°C.

Temperature (°C)	Magnetic Saturation (emu/g)
700	59.9
900	61.9

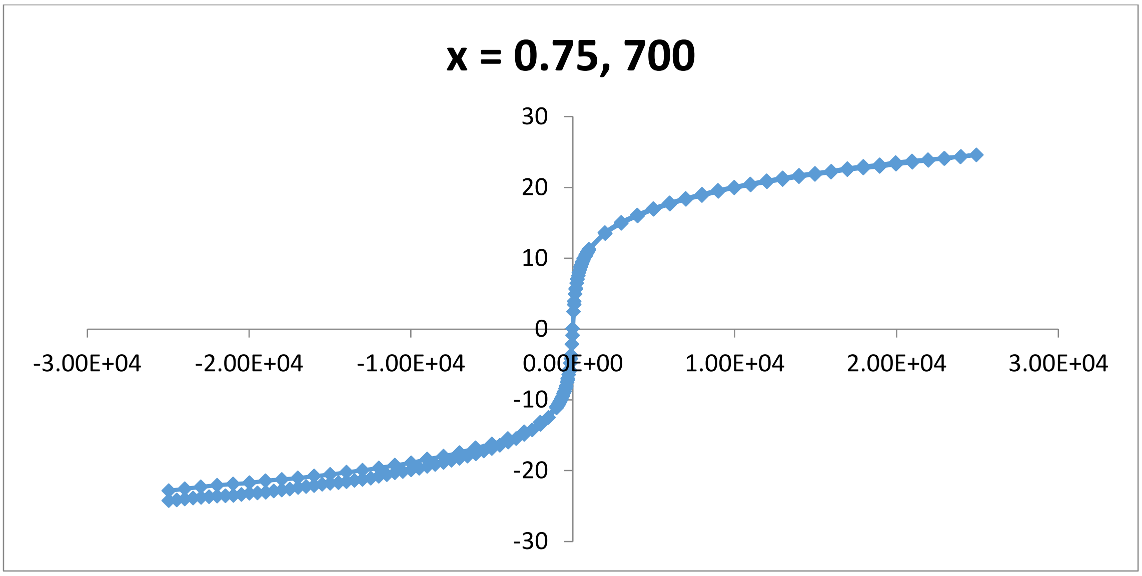

Figure 4.22: Result VSM for X=0.75 at 700˚C

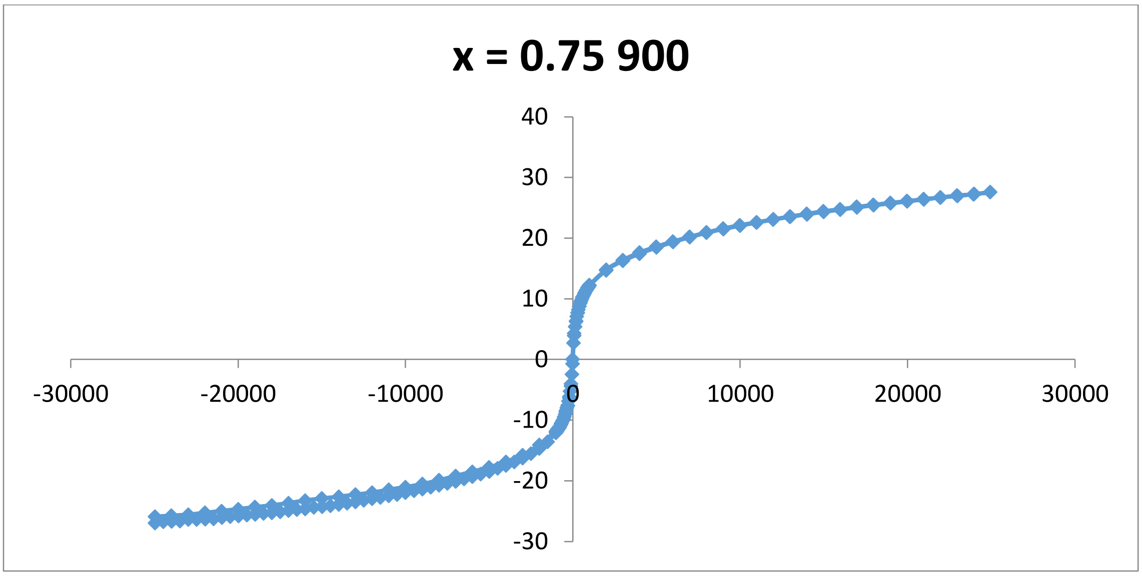

Figure 4.23: Result VSM for X=0.75 at 900˚C

The figure 4.22 and figure 4.23 shows the magnetic saturation of the sample, $Ni_{0.25}Zn_{0.75}Fe_2O_4$ (X=0.75) of two different temperature which are 700˚C and 900˚C.

Temperature (˚C)	Magnetic Saturation (emu/g)
700	24.6
900	27.6

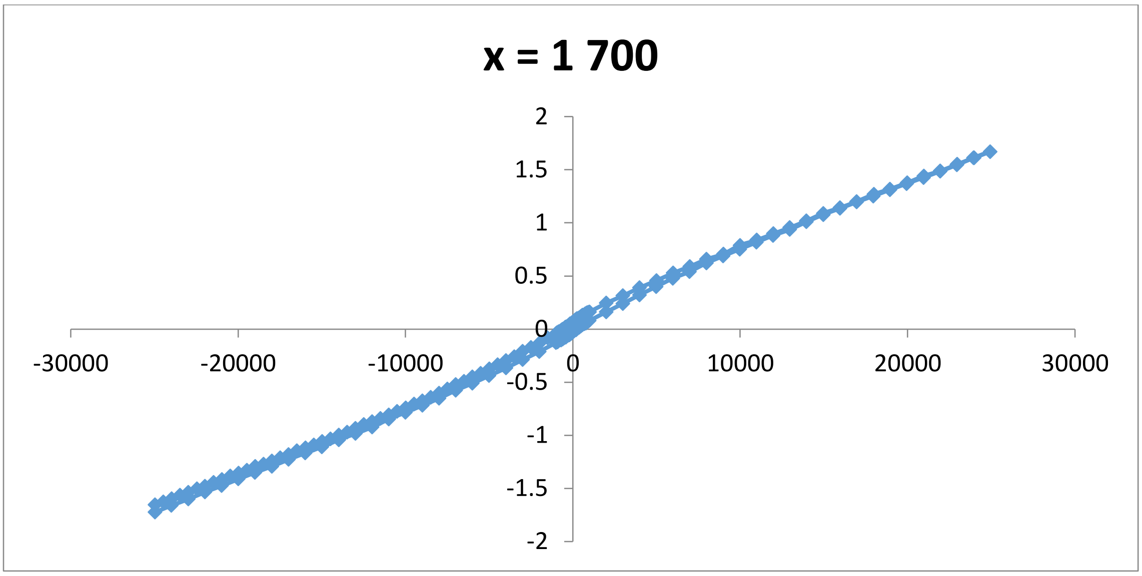

Figure 4.24: Result VSM for X=1 at 700˚C

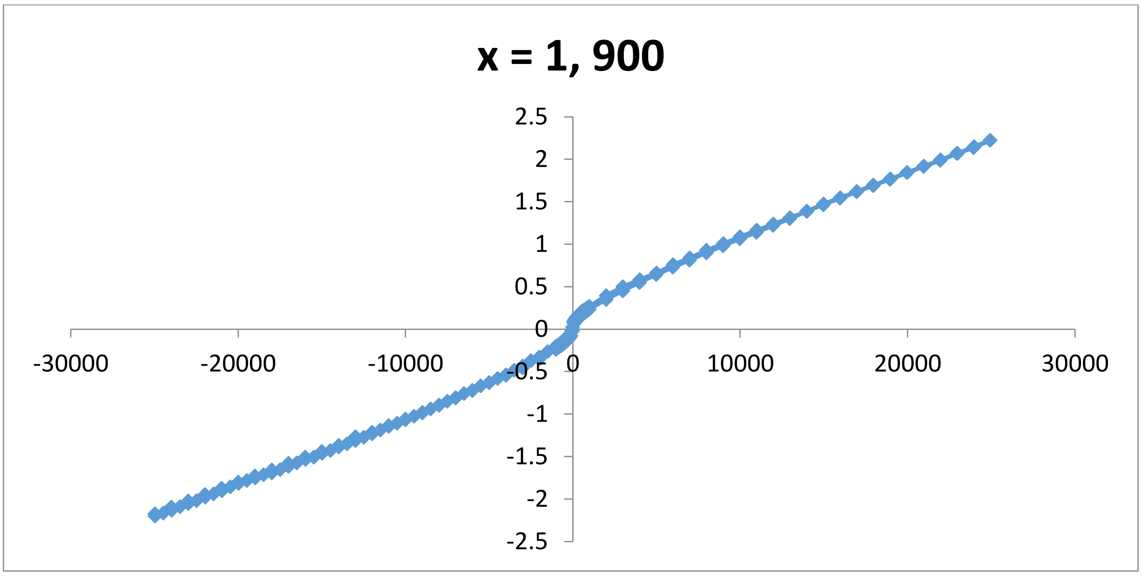

Figure 4.25: Result VSM for X=1 at 900˚C

The figures 4.24 and figure 4.25 shows the magnetic saturation of the sample, Zn Fe_2O_4 (X=1) of two different temperature which are 700˚C and 900˚C.

Temperature (˚C)	Magnetic Saturation (emu/g)
700	16.7
900	22.2

The table below show the summary of the magnetic saturation of both temperature of all the samples.

Table 4.2: Magnetic Saturation of each samples

Samples	Magnetic Saturation (emu/g)	
	Temperature: **700** $^{\circ}$C	Temperature: **900** $^{\circ}$C
X=0	20.3	21.6
X=0.25	58.9	59.2
X=0.5	59.9	61.9
X=0.75	24.6	27.6
X=1	16.7	22.2

The highest magnetization based on the annealing temperature will be selected for proceeding to the next stage which is the core-flooding experiment. Based on the result, the higher the annealing temperature will give more magnetic saturation of the nanoparticles.

Next, the samples which are annealed at 900°C will be chosen since it has higher magnetic saturation than samples annealed at 700°C. The samples will be injected into the core sample (sand beads) in the form of nanofluid after being immersed and prepared with deionised water.

4.1.4 Field Emission Scanning Electron Microscope (FESEM) Results

4.1.4.1 Sample X=0

Figure 4.26 show the microscope image of grain of the sample Nickel-Zinc-Ferrites nanoparticles that are annealed at 900˚C.

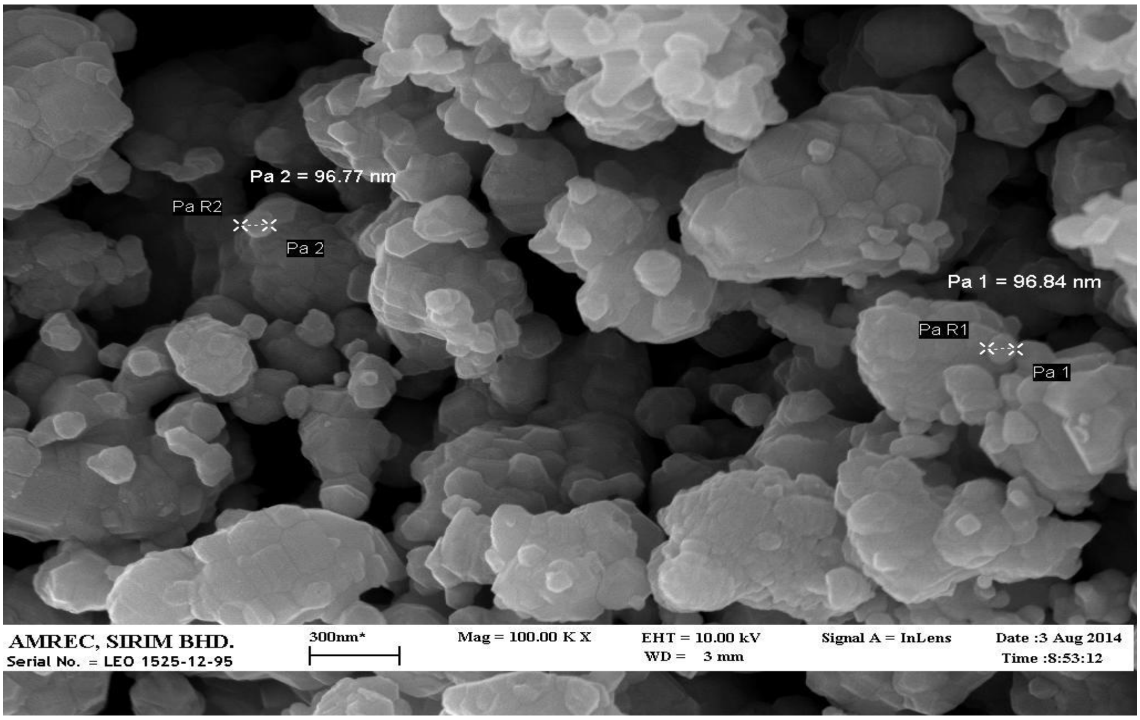

Figure 4.26: FESEM Results for X=0 at 100K Magnification

From the figure 4.26, it can be observed that the grain size is at range from 96.77 – 98.64 nm. It shows the irregular shape.

4.1.4.2 Sample X=0.25

Figure 4.27 shows the microscope image of grain of the sample Nickel-Zinc-Ferrites nanoparticles that are annealed at 900°C.

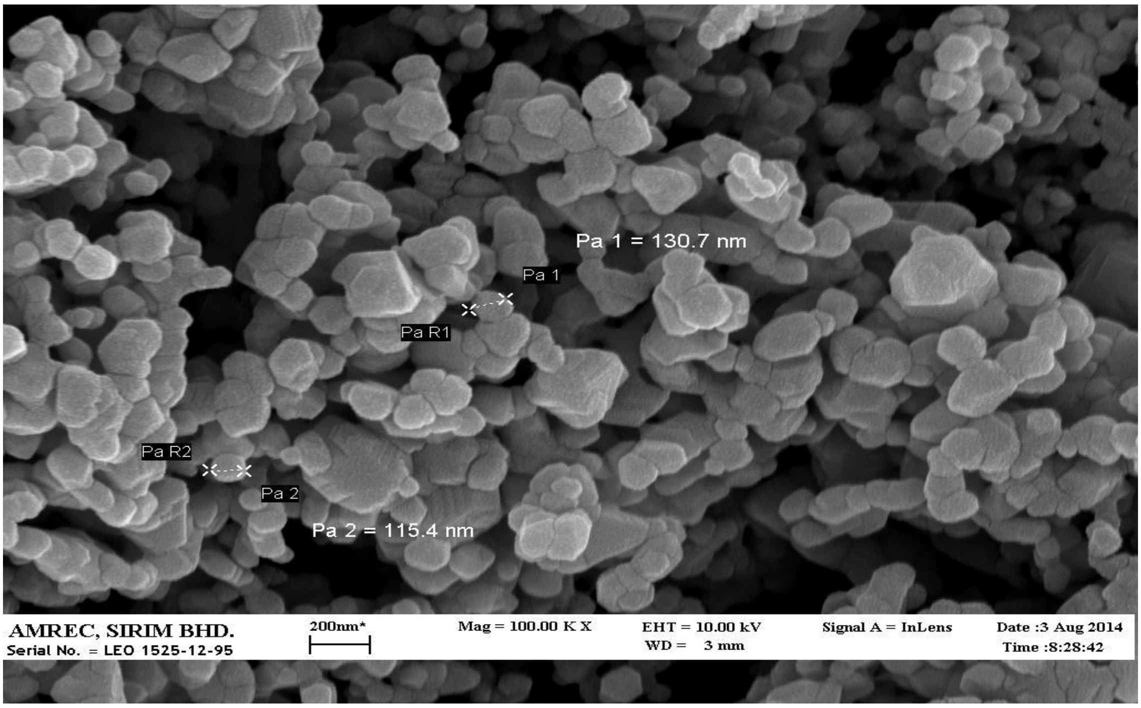

Figure 4.27: FESEM Results for X=0.25 at 100K Magnification

From the figure 4.27, it can be observed that the grain size is at range from 115.4-130.7 nm. It shows the irregular shape of grain.

4.1.4.3 Sample X=0.5

Figure 4.28 show the microscope image of grain of the sample Nickel-Zinc-Ferrites nanoparticles that are annealed at 900°C.

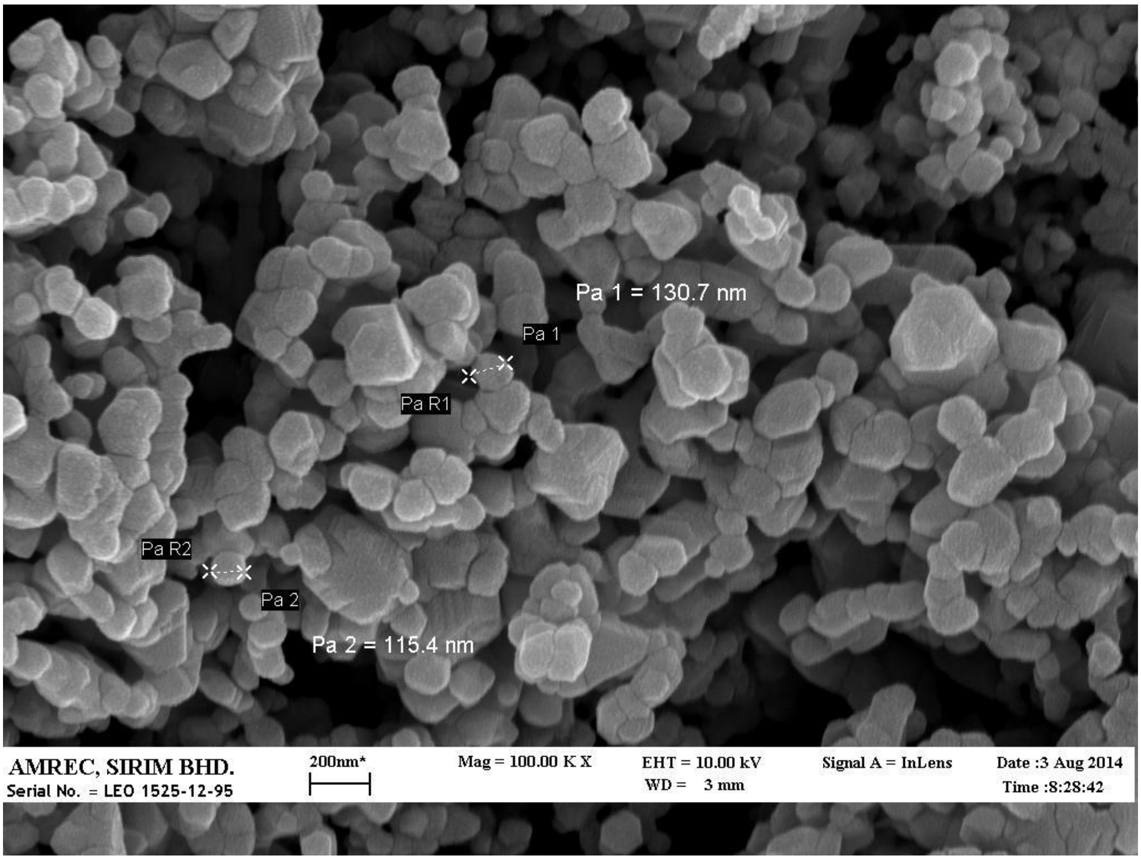

Figure 4.28: FESEM Results for X=0.5 at 100K Magnification

From the figure 4.28, it can be observed that the grain size is at range from 119.1–103.3 nm. It shows the irregular shape.

4.1.4.4 Sample X=0.75

Figure 4.29 show the microscope image of grain of the sample Nickel-Zinc-Ferrites nanoparticles that are annealed at 900°C.

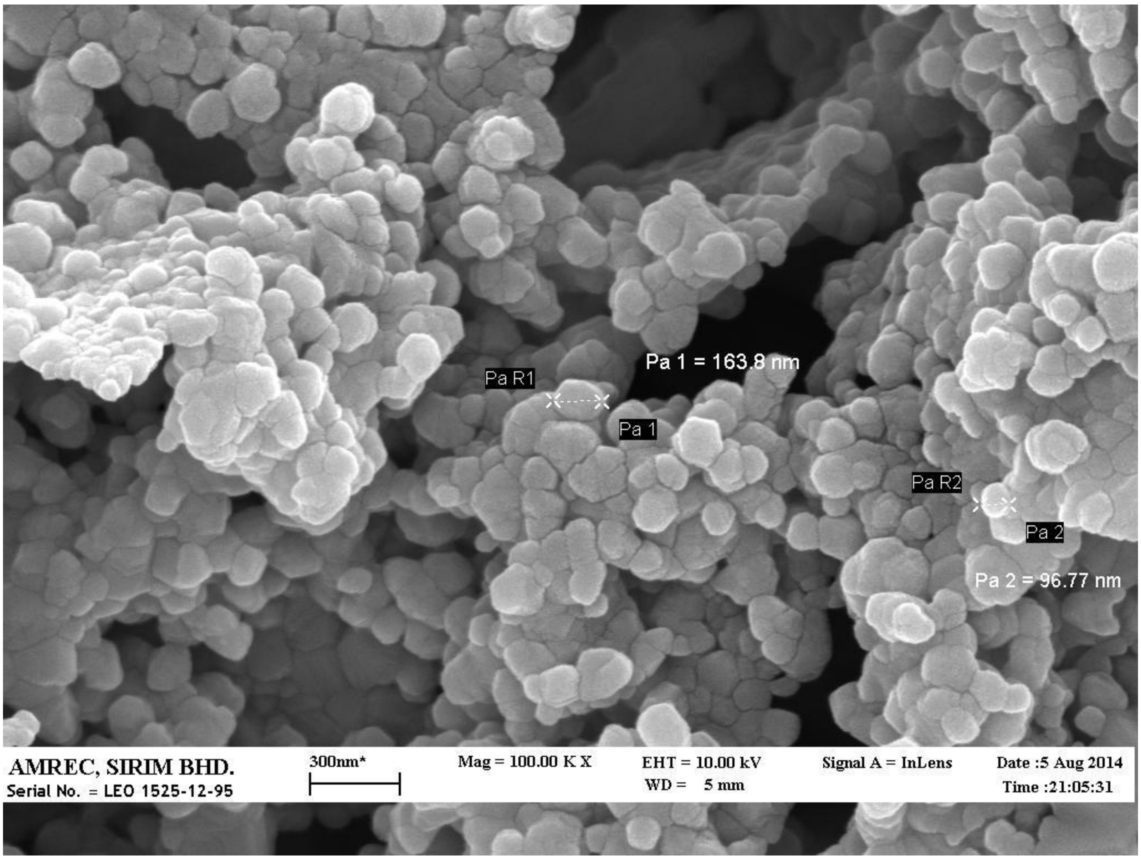

Figure 4.29: FESEM Results for X=0.75 at 100K Magnification

From the figure 4.29, it can be observed that the grain size is at range from 96.77–163.9 nm. It shows the irregular shape.

4.1.4.4 Sample X=0.1

Figure 4.30 show the microscope image of grain of the sample Nickel-Zinc-Ferrites nanoparticles that are annealed at 900°C.

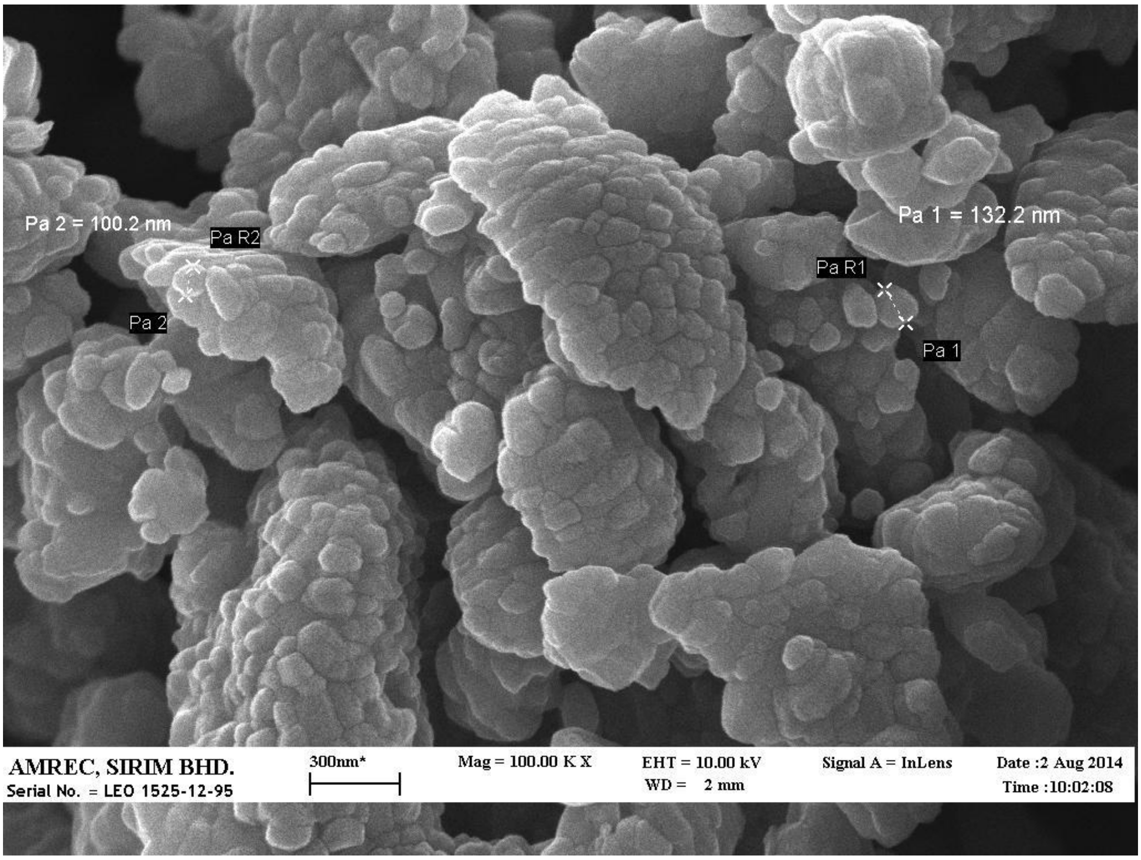

Figure 4.30: FESEM Results for X=1 at 100K Magnification

From the figure 4.30, it can be observed that the grain size is at range from 100.2-132.2 nm. It shows the irregular shape.

4.1.5 Core-Flooding Experiment Results

The core flooding experiment has been conducted to test the effect of nanoparticles on Enhanced Oil Recovery which means how much oil can be recovered after injecting the nanofluid into the core sample. The core sample consists of two different sizes of glass bead using the setup apparatus as shown in the methodology part.

Consistently, about two pore volume has been injected into the core sample. This is to make sure 1 pore volume is to push the oil from the pore space and another 1 pore volume to make sure the nanofluid has already saturated in the core sample. The figure 4.31 show the crude oil that recover from the glass bead using two pore volume injection of nanofluid. The reading is taken at every 0.2 pore volume to see the relationship between the pore volume and also the oil recovery percentage.

Figure 4.31: Crude Oil recover in Nanofluid Injection

4.1.5.1 Sample X=0

The table 4.3 show the data for the experiments that carried out using the sample X=0, $Ni_1\ Fe_2\ O_4$

Table 4.3: The injection sequence for X=0

Brine Injection	
Flow rate (mL/min)	1.0
Dry weight of the core sample (g)	774
Wet weight of the core sample (g)	803
Δ weight (g)	29
Density of the brine (g/cm^3)	1.005
pressure (psi)	0.22
Pore Volume (mL)	28.86
2PV (mL)	57.71
Oil injection	
Flow rate (mL/min)	0.8
pressure (psi)	0.75
Original Oil in Place, OOIP (mL)	25
Water Flooding (Secondary Recovery)	
Flow rate (mL/min)	1.0
Pressure (psi)	0.53
Volume of Oil Recovered (mL)	10
Nanofluid Injection (EOR)	
Concentration (wt. %)	0.1
Flow rate (mL/min)	1.0
Average Pressure during injection (psi)	0.34

The table 4.4 show the data when injecting the nanofluid as Tertiary Recovery. Two pore volume of nanofluid has been injected into the core sample to see how much oil can be recovered.

Table 4.4: The Nanofluid Injection Data for X=0

Pore Volume	Δ Pressure (psi)	Volume of Oil Recovered (mL)	Cumulative Recovery (mL)	Percentage Recovery (%)
0.2	0.38	0.1	0.1	0.67
0.4	0.34	0.2	0.3	2.00
0.6	0.36	0.15	0.45	3.00
0.8	0.3	0.2	0.65	4.33
1.0	0.34	0.25	0.9	6.00
1.2	0.38	0.25	1.15	7.67
1.4	0.36	0.25	1.4	9.33
1.6	0.32	0.05	1.45	9.67
1.8	0.32	0	1.45	9.67
2.0	0.32	0	1.45	9.67

From the data in table 4.4, it is observed that the sample X=0 is recover almost 9.7% of oil from the Residual Oil in Place (ROIP) which is about 1.45 mL. The figure 4.32 show the trending of the recovery of oil and the pore volume injected.

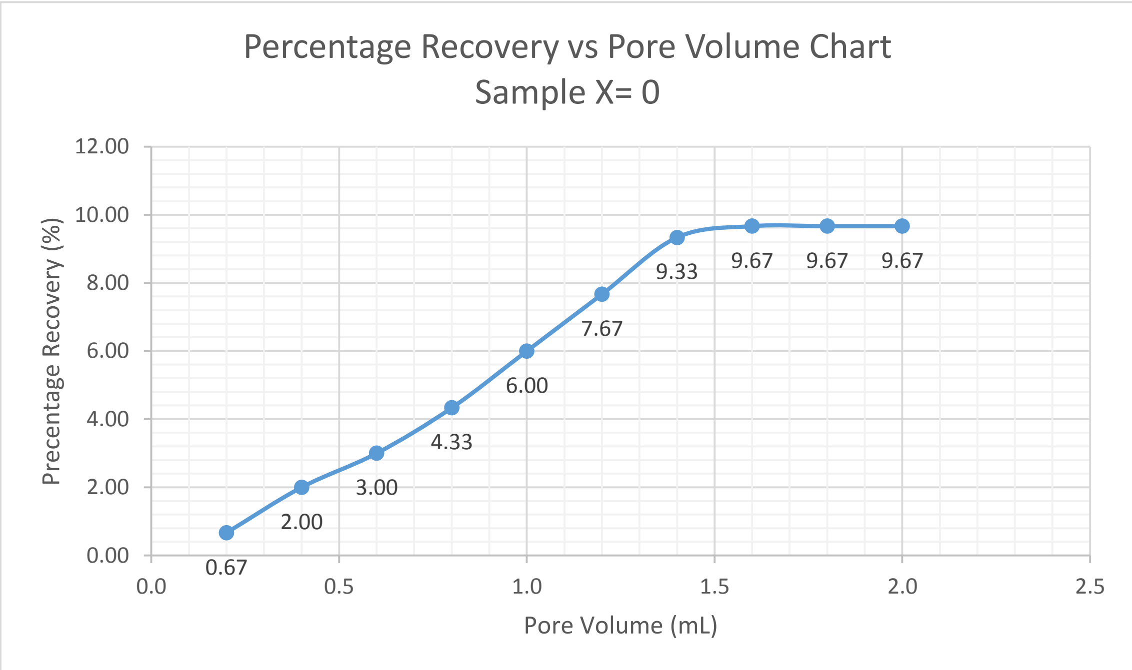

Figure 4.32: Percentage Recovery vs Pore Volume Chart for X=0

4.1.4.2 Sample X=0.25

The table 4.5 show the data for the experiments that carried out using the sample X=0.25, $Ni_{0.75}$ $Zn_{0.25}$ Fe_2 O_4.

Table 4.5: The injection sequence for X=0.25

Brine Injection	
Flow rate (mL/min)	1.0
Dry weight of the core sample (g)	778
Wet weight of the core sample (g)	806
Δ weight (g)	28
Density of the brine (g/cm³)	1.005
pressure (psi)	0.27
Pore Volume (mL)	27.86
2PV (mL)	55.72
Oil injection	
Flow rate (mL/min)	0.8
pressure (psi)	0.78
Original Oil in Place, OOIP (mL)	25
Water Flooding (Secondary Recovery)	
Flow rate (mL/min)	1.0
Pressure (psi)	0.54
Volume of Oil Recovered (mL)	10
Nanofluid Injection (EOR)	
Concentration (wt. %)	0.1
Flow rate (mL/min)	1.0
Average Pressure during injection (psi)	0.35

The table 4.6 show the data recorded when injecting the nanofluid as Tertiary Recovery.

Table 4.6: The Nanofluid Injection Data for X=0.25

Pore Volume	∆ Pressure (psi)	Volume of Oil Recovered (mL)	Cumulative Recovery (mL)	Percentage Recovery (%)
0.2	0.38	0.1	0.1	0.67
0.4	0.42	0.15	0.25	1.67
0.6	0.46	0.15	0.4	2.67
0.8	0.42	0.2	0.6	4.00
1.0	0.45	0.25	0.85	5.67
1.2	0.46	0.25	1.1	7.33
1.4	0.46	0.25	1.35	9.00
1.6	0.48	0.1	1.45	9.67
1.8	0.40	0.1	1.55	10.33
2.0	0.41	0	1.55	10.33

From the data in table 4.6, it is observed that the sample X=0.25 is recover almost 10.4% of oil from the Residual Oil in Place (ROIP) which is about 1.55 mL. The figure 4.33 show the trending of the recovery of oil and the pore volume injected.

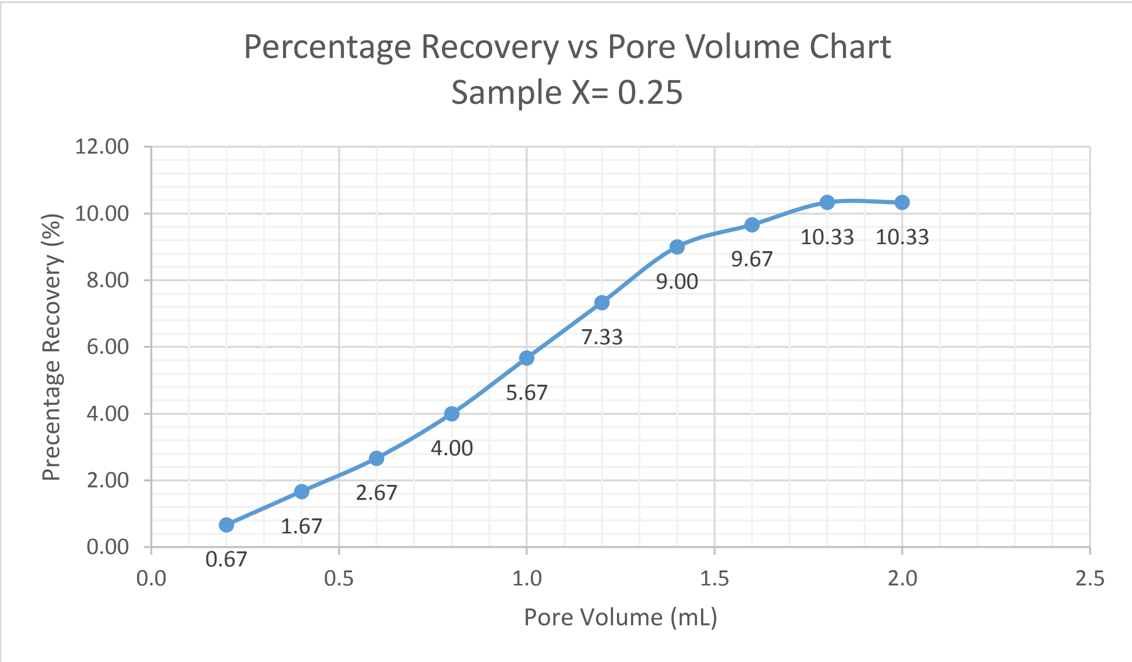

Figure 4.33: Percentage Recovery vs Pore Volume Chart for X=0.25

4.1.4.3 Sample X=0.5

The table 4.7 show the data for the experiments that carried out using the sample X=0.5, $Ni_{0.5} Zn_{0.5} Fe_2 O_4$.

Table 4.7: The injection sequence for X=0.5

Brine Injection	
Flow rate (mL/min)	1.0
Dry weight of the core sample (g)	778
Wet weight of the core sample (g)	806
Δ weight (g)	28
Density of the brine (g/cm³)	1.005
pressure (psi)	0.27
Pore Volume (mL)	27.86
2PV (mL)	55.72
Oil injection	
Flow rate (mL/min)	0.8
pressure (psi)	0.78
Original Oil in Place, OOIP (mL)	25
Water Flooding (Secondary Recovery)	
Flow rate (mL/min)	1.0
Pressure (psi)	0.53
Volume of Oil Recovered (mL)	10
Nanofluid Injection (EOR)	
Concentration (wt. %)	0.1
Flow rate (mL/min)	1.0
Average Pressure during injection (psi)	0.35

The table 4.8 show the data recorded when injecting the nanofluid as Tertiary Recovery.

Table 4.8: The Nanofluid Injection Data for X=0.5

Pore Volume	Δ Pressure (psi)	Volume of Oil Recovered (mL)	Cumulative Recovery (mL)	Percentage Recovery (%)
0.2	0.32	0.15	0.15	1.00
0.4	0.29	0.2	0.35	2.33
0.6	0.35	0.25	0.6	4.00
0.8	0.36	0.3	0.9	6.00
1.0	0.42	0.3	1.2	8.00
1.2	0.4	0.3	1.5	10.00
1.4	0.36	0.4	1.9	12.67
1.6	0.32	0.25	2.15	14.33
1.8	0.32	0.15	2.3	15.33
2.0	0.3	0.1	2.4	16.00

From the data in table 4.8, it is observed that the sample X=0.5 is recover almost 16% of oil from the Residual Oil in Place (ROIP) which is about 2.4 mL. The figure 4.34 show the trending of the recovery of oil and the pore volume injected.

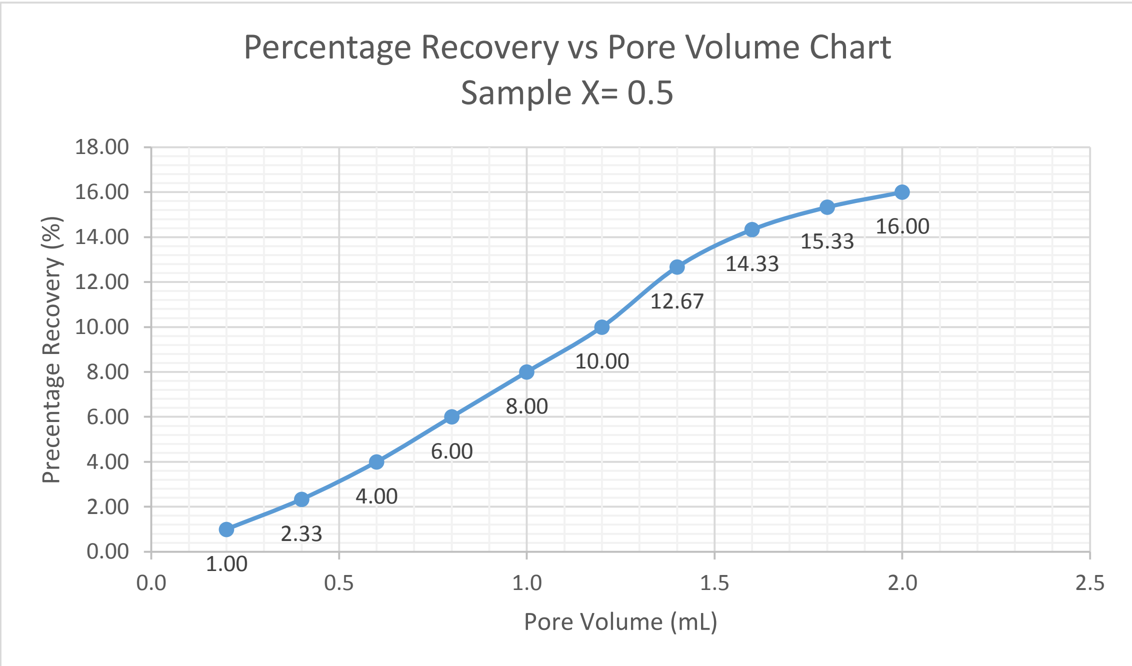

Figure 4.34: Percentage Recovery vs Pore Volume Chart for X=0.5

4.1.4.4 Sample X=0.75

The table 4.9 show the data for the experiments that carried out using the sample X=0.75, $Ni_{0.25}Zn_{0.75}Fe_2O_4$.

Table 4.9: The injection sequence for X=0.75

Brine Injection	
Flow rate (mL/min)	1.0
Dry weight of the core sample (g)	784
Wet weight of the core sample (g)	818
Δ weight (g)	29
Density of the brine (g/cm³)	1.005
pressure (psi)	0.27
Pore Volume (mL)	28.9
2PV (mL)	57.8
Oil injection	
Flow rate (mL/min)	0.8
pressure (psi)	0.78
Original Oil in Place, OOIP (mL)	25
Water Flooding (Secondary Recovery)	
Flow rate (mL/min)	1.0
Pressure (psi)	0.52
Volume of Oil Recovered (mL)	10
Nanofluid Injection (EOR)	
Concentration (wt. %)	0.1
Flow rate (mL/min)	1.0
Average Pressure during injection (psi)	0.34

The table 4.10 show the data recorded when injecting the nanofluid as Tertiary Recovery.

Table 4.10: The Nanofluid Injection Data for X=0.75

Pore Volume	Δ Pressure (psi)	Volume of Oil Recovered (mL)	Cumulative Recovery (mL)	Percentage Recovery (%)
0.2	0.32	0.1	0.1	0.67
0.4	0.29	0.15	0.25	1.67
0.6	0.35	0.15	0.4	2.67
0.8	0.36	0.2	0.6	4.00
1.0	0.42	0.2	0.8	5.33
1.2	0.4	0.2	1	6.67
1.4	0.36	0.2	1.2	8.00
1.6	0.32	0.2	1.4	9.33
1.8	0.32	0.1	1.5	10.00
2.0	0.3	0.05	1.55	10.33

From the data in table 4.10, it is observed that the sample X=0.75 is recover almost 10.3% of oil from the Residual Oil in Place (ROIP) which is about 1.55 mL. The figure 4.35 show the trending of the recovery of oil and the pore volume injected.

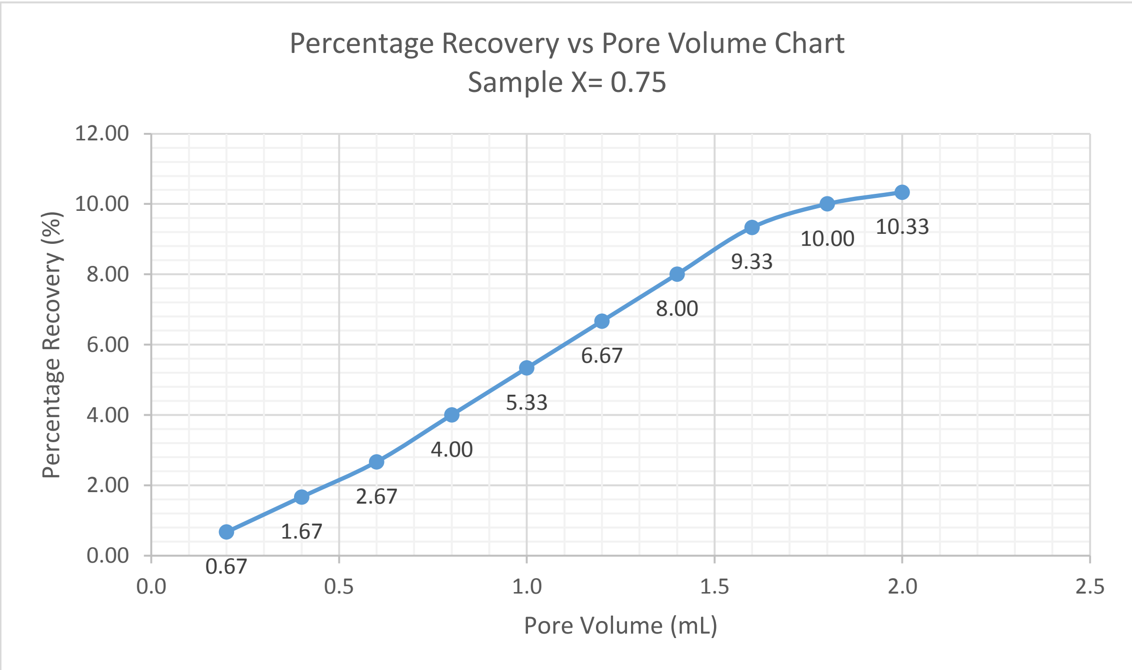

Figure 4.35: Percentage Recovery vs Pore Volume Chart for X=0.75

4.1.4.5 Sample X=0.1

The table 4.11 show the data for the experiments that carried out using the sample X=1, Zn Fe_2 O_4.

Table 4.11: The injection sequence for X=1

Brine Injection	
Flow rate (mL/min)	1.0
Dry weight of the core sample (g)	788
Wet weight of the core sample (g)	816
Δ weight (g)	28
Density of the brine (g/cm^3)	1.005
pressure (psi)	0.26
Pore Volume (mL)	27.9
2PV (mL)	55.8
Oil injection	
Flow rate (mL/min)	0.8
pressure (psi)	0.79
Original Oil in Place, OOIP (mL)	25
Water Flooding (Secondary Recovery)	
Flow rate (mL/min)	1.0
Pressure (psi)	0.53
Volume of Oil Recovered (mL)	10
Nanofluid Injection (EOR)	
Concentration (wt. %)	0.1
Flow rate (mL/min)	1.0
Average Pressure during injection (psi)	0.35

The table 4.12 show the data recorded when injecting the nanofluid as Tertiary Recovery.

Table 4.11: The Nanofluid Injection Data for X=1

Pore Volume	Δ Pressure (psi)	Volume of Oil Recovered (mL)	Cumulative Recovery (mL)	Percentage Recovery (%)
0.2	0.29	0.1	0.1	0.67
0.4	0.32	0.15	0.25	1.67
0.6	0.36	0.15	0.4	2.67
0.8	0.36	0.25	0.65	4.33
1.0	0.38	0.3	0.95	6.33
1.2	0.4	0.3	1.25	8.33
1.4	0.32	0.25	1.5	10.00
1.6	0.37	0.2	1.7	11.33
1.8	0.36	0.1	1.8	12.00
2.0	0.31	0.1	1.9	12.67

From the data in table 4.11, it is observed that the sample X=1 is recover almost 12.7% of oil from the Residual Oil in Place (ROIP) which is about 1.9 mL. The figure 4.36 show the trending of the recovery of oil and the pore volume injected.

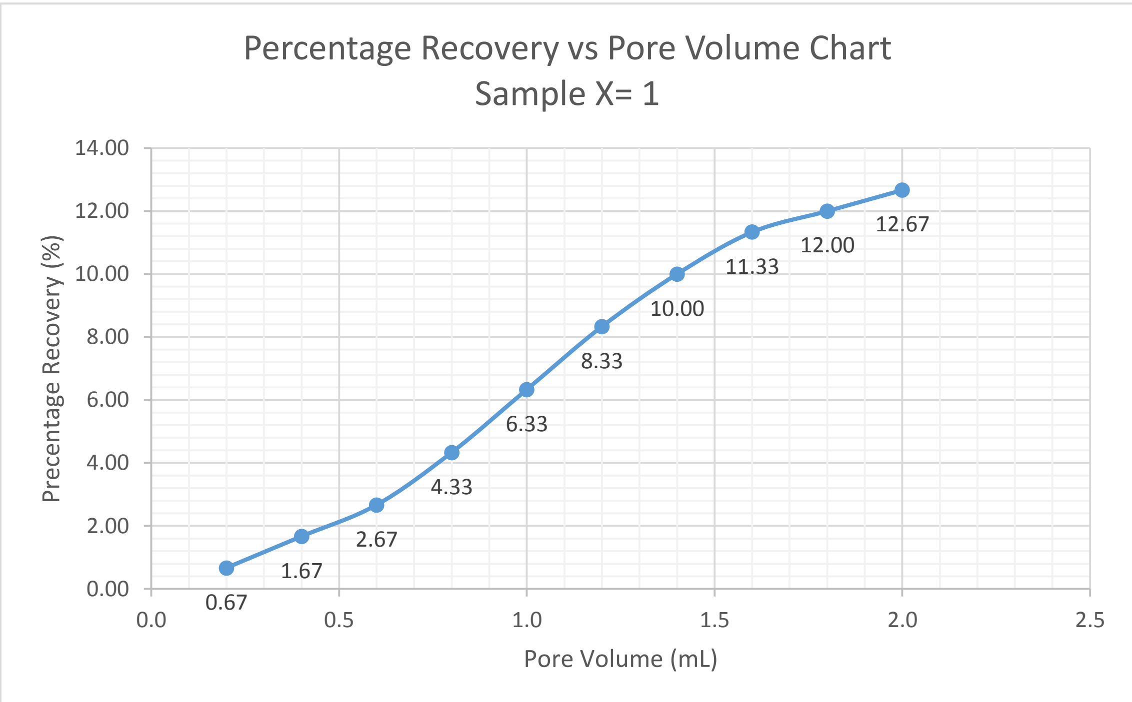

Figure 4.36: Percentage Recovery vs Pore Volume Chart for X=1

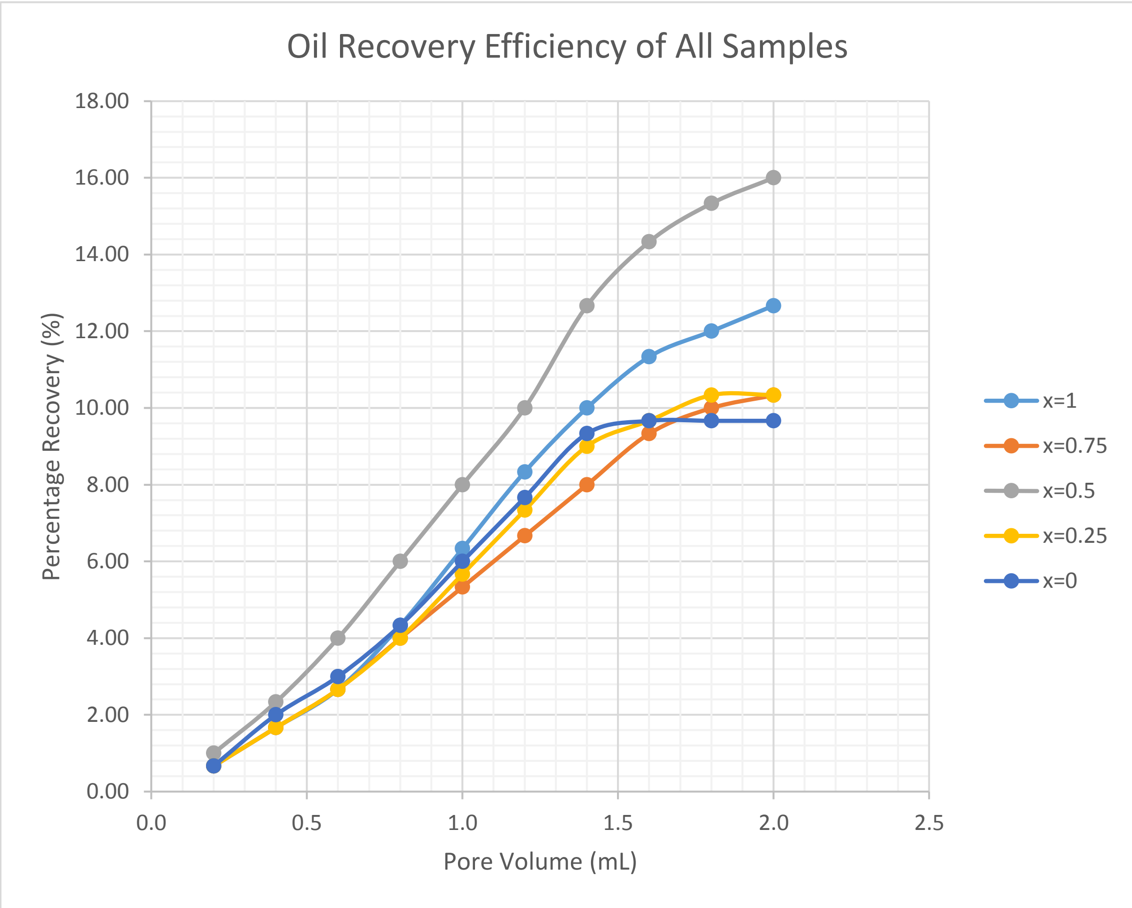

Figure 4.37: The Summary of the Percentage Recovery vs Pore Volume Chart for all samples

The figure 4.37 show the oil percentage recovery from all the five samples. From the graph, the highest oil percentage recovery recorded by sample x=0.5 which is equal to 16% of oil in the core sample. This show the better ratio in Nickel to Zinc give better magnetisation which result in better oil recovery.

4.2 Discussion

The Sol-Gel method is the simplest method to synthesis the Nickel-Zinc-Ferrites nanoparticles. This method only involved a simple procedures that are easy to understand and follow. The tools used in this method includes the hot plate for heating, magnetic stirrer, fume hood and also the heating oven. This experiment is conducted carefully in a lab and all heating process is done in the fume hood. All the safety measures are already taken into account.

All the 10 samples are being fully synthesized using this method; Sol-Gel method. The samples consist of different ratio of nickel to zinc which are x=0 (nickel 0: zinc 1), x=0.25 (nickel 3: zinc 1), x=0.5 (nickel 1: zinc 1), x =0.75 (nickel 1: zinc 3) and x=1(nickel 1: zinc 0). All the samples have been annealed at two different temperature which are at 700°C and 900°C for each composition. At the end of the day, there are 10 samples have been synthesized. All the samples were characterized using XRD, VSM and FESEM. The XRD results shows the indication of purely nickel zinc ferrites when matching to it standard card at different ratio. While, the VSM result will show the magnetic saturation of each samples. The highest magnetic saturation for each variant of composition has been recorded with the samples annealed at 900°C. These samples are prepared to be nanofluid to be injected in the core sample (sand beads) in the core-flooding experiment. This experiment will evaluate the oil recovery efficiency based on the effect of different magnetization of each nickel to zinc ratio.

The figure 12 to figure 22 above show the result of XRD Characterization. The sample X=0.25, 0.5 and 0.75 shows the required peak that are matching with the standard card according to its ratio of Nickel to Zinc. This shows that the sample prepared are pure Nickel Zinc Ferrite.On the other hand, the sample X=0 and X=1 shows additional peak which mean different from the standard card indicates the samples are not purely Nickel Zinc Ferrite. This is because in sample X=0 there are no Nickel element so it cannot follow the standard card of Nickel Zinc Ferrite while in sample X=1 there are no Zinc element thus it also cannot follow the standard card of Nickel Zinc Ferrite.

For VSM results, the hysteresis graph are obtained for almost samples annealed at 700°C and 900°C. Based on the result in the figure 23 until figure 32 above, the samples X=0.5 which contain 1:1 Nickel to Zinc ratio shows the highest magnetization which are 59.9 emu/g at 700°C and 61.9 emu/g at 900°C compare to the other sample. Other than that, from the result also, the magnetic saturation of samples annealed at 700°C is lower than the samples annealed at 900°C. Thus, the higher the annealing temperature the higher the magnetic saturation.

From the FESEM results, the size particles of the nanoparticles ranging from 96.77-163.9 nm. The sample X=0 achieved the smallest size of particles which is about 96.77-98.64nm. Besides, the size of the particle sample that give the highest oil recovery is ranging from 119.1-130.3nm. Although the size is slightly bigger than sample X=0, it is still give better recovery of oil. Thus, the magnetisation effect is play an important effect to the recovery of oil compared to the size of the particle of the nanoparticles. In all samples shows irregular shape and the image is captured at100K magnification.

Since the samples annealed at 900°C yield better magnetization, this sample will be immersed into deionised water to form nanofluid. The nanofluid will be ultrasonicated for one hours to make sure the nanoparticles is dispersed well in the deionised water. The procedure of conducting the experiment is already stated in methodology part. The core samples is filled with two different sizes of glass bead to achieve better sorting arrangement of particles. However, the core characteristics need to be defined as it is simulate the condition of the real reservoir. The parameters such as the porosity and permeability are the important parameters that need to be determined. The author did not measure the porosity and permeability of the core samples however to further study on this research, recommendation has been made to increase the efficiency of the core-flooding experiment.

From the experiment conducted, the sample X=0.5 shows better oil recovery percentage from Residual Oil in Place (ROIP) which is about 16%. This sample also has shown highest magnetisation thus the relationship of magnetisation and oil recovery percentage can be made. The better the magnetisation, the higher oil recovery percentage. The magnetization of the nanoparticles will enhanced the viscosity of the nanofluid by interaction between the nanoparticles. Meanwhile, the lowest recovery percentage is 9.67% that was achieved using the sample X=0.

The dispersion of nanoparticles inside the dispersing fluid is actually increase its viscosity. The nanoparticles suspension will make the fluid more viscous to be injected into the core sample. When the nanofluid in contact with the crude oil, it can prevent the early breakthrough or fingering effect thus make the nanofluid more efficient in pushing the oil to be produced. In order to get the piston-like displacement inside the pore space, the viscosity of the nanofluid has to be more viscous than the oil to ensure the oil can be push to the production zone.

The recommendation part in this report state the recommendations to this study and experiment in order to have a better and efficient result.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The nanoparticles study is very useful in EOR hence all the researcher in the world have been developed many techniques especially to encounter the problem to extract the oil. The unique characteristics is very useful in EOR to improve certain physical and chemical properties of fluids so that oil in the pores can easy move to the production zone.

The five samples which contain different ratio of Nickel to Zinc were synthesized using the Sol-Gel method. The sample were annealed at two different annealing temperature, 700^{O}C and 900^{O}C. The selected temperature is chosen based on the result of TGA Analysis which showing the optimum annealing temperature of the samples. Then, the samples were tested using VSM Testing to measure the magnetization. The samples at each composition annealed at 900^{O}C shows better magnetization then the samples will be chosen in the core-flooding experiment to test the oil recovery efficiency.

The sample X=0.5 has shown the highest recovery efficiency which is about 16% from the ROIP. This show the better ratio of nickel to zinc is 1 to 1. This sample sizes is ranging from 119.1-130.3nm. The particle sizes is captured at 100K magnification and it shows irregular shape of nanoparticles. Apart from that, the lowest oil recovery efficiency which is about 9.67%, achieved by sample X=0. Thus, the author has concluded that the better the magnetisation will result in better oil recovery.

This research and study are very useful for the EOR future and also for oil and gas business. The demand of oil is keep increasing each day and surely the best economical method to extract oil from reservoir will be applied by the engineer in order to meet the demand and also economic benefit.

5.2 Recommendation

The recommendation and suggested expansion for future work for this research are to study different type of magnetic nanoparticles in EOR recovery efficiency so that we can know which type of magnetic nanoparticles can yield optimum oil recovery. This research is only focusing on Nickel Zinc Ferrite nanoparticles and the other magnetic nanoparticles also need to be tested to see the different of magnetization and type of magnetic nanoparticles.

Besides, the relevancy of using the magnetic nanoparticles as EOR agents need to be tested in the real field whether surely it can helps in oil recovery. All the require data need to be present in order to test the real effectiveness of nanofluid injection a real reservoir. Other than that, the cost optimisation also need to achieve when optimising the production of the oil in order to maximise the profit.

The experiment conducted need to take all the factors to make sure the successfully of this research. The synthesising of nanofluid need to be done carefully to have the expected result. The nanoparticles need to be tested by different test in order to make sure the content of the nanoparticles.

For the core-flooding experiment, it is essential to measure the core sample properties such as porosity and permeability. Thus, in order to continue this research, the author recommend to measure the properties of the core samples and also the properties of the glass beads in order to have a better result of the oil recovery efficiency.

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APPENDICES

Nickel-Zinc-Ferrite Chemical Composition Calculation

x = 0

$Ni_{1-x}\,Zn_x\,Fe_2\,O_4 \rightarrow NiFe_2O_4$

Chemical equation:

$$Ni\,(NO_3)_2.6H_2O + 2Fe\,(NO_3)_3\,.9H_2O \rightarrow NiFe_2O_4 + volatiles$$

Sample targeted mass = 20g

No. of moles NZFE = $\frac{m}{MW} = \frac{20g}{[58.6934]+2[55.845]+4[15.9999]}$

= 0.0853 mol

From the chemical equation, 1 *mol of* Ni $(NO_3)_2.6H_2O$ is needed to produce 1 mol of $NiFe_2O_4$

n $Ni_R = \frac{1\,mol\,of\ \text{NiR}}{1\,mol\,NiFe2O4}$ x 0.0853 mol of $NiFe_2O_4$

= 0.0853 mol

m Ni_R = n Ni_R x MW Ni_R
= 0.0853 x 290.801 = <u>24.8053g</u>

From the chemical equation, *2 mol of Fe* $(NO_3)_3\,.9H_2O$ is needed to produce 1 mol of $NiFe_2O_4$

= $\frac{2\,mol}{1\,mol\,of\,NiFe2O4}$ x 0.0853 mol of $NiFe_2O_4$

= 0.1706 mol

m Fe_R = n Fe_R x MW Fe_R
= 0.1706 x 404.0388 = <u>68.929g</u>

x = 0.25

$Ni_{1-x} Zn_x Fe_2 O_4 \rightarrow Ni_{0.75} Zn_{0.25} Fe_2O_4$

Chemical equation:

$0.75Ni (NO_3)_2.6H_2O + 0.25Zn (NO_3)_2.6H_2O + 2Fe (NO_3)_3 .9H_2O \rightarrow Ni_{0.75} Zn_{0.25} Fe_2O_4$ + *volatiles*

Sample targeted mass = 20g

No. of moles NZFE = $\frac{m}{MW} = \frac{20g}{0.75[58.6934]+0.25[65.409]+2[55.845]+4[15.9999]}$

= 0.0847 mol

From the chemical equation, *0.75 mol of* $Ni (NO_3)_2.6H_2O$ is needed to produce 1 mol of *NZFE*

n Ni_R = $\frac{0.75\, mol}{1\, mol\, NZFE}$ x 0.0847 mol of *NZFE*

= 0.0635 mol

m Ni_R = n Ni_R x MW Ni_R

= 0.0635 x 290.801 = <u>18.4659g</u>

From the chemical equation, *0.25 mol of* $Zn (NO_3)_2.6H_2O$ *is* needed to produce 1 mol of *NZFE*

= $\frac{0.25\, mol}{1\, mol\, of\, NZFE}$ x 0.0847 mol of *NZFE*

= 0.0212 mol

m Fe_R = n Fe_R x MW Fe_R

= 0.0212 x 297.5166 = <u>6.3074g</u>

From the chemical equation, *2 mol of* $Fe (NO_3)_3 .9H_2O$ is needed to produce 1 mol of *NZFE*

= $\frac{2\, mol}{1\, mol\, of\, NZFE}$ x 0.0847 mol of *NZFE*

= 0.1694 mol

m Fe_R = n Fe_R x MW Fe_R

= 0.1694 x 404.0388 = <u>68.444</u>

x = 0.5

$Ni_{1-x}Zn_xFe_2O_4 \rightarrow Ni_{05}Zn_{0.5}Fe_2O_4$

Chemical equation:

$$0.5Ni(NO_3)_2.6H_2O + 0.5Zn(NO_3)_2.6H_2O + 2Fe(NO_3)_3.9H_2O \rightarrow Ni_{05}Zn_{0.5}Fe_2O_4 + volatiles$$

Sample targeted mass = 20g

No. of moles NZFE = $\frac{m}{MW} = \frac{20g}{0.5[58.6934]+0.5[65.409]+2[55.845]+4[15.9999]}$

= 0.0841 mol

From the chemical equation, *0.5 mol of* $Ni(NO_3)_2.6H_2O$ is needed to produce 1 mol of *NZFE*

n Ni_R = $\frac{0.5\ mol}{1\ mol\ NZFE}$ x 0.0841 mol of *NZFE*

= 0.0421 mol

m Ni_R = n Ni_R x MW Ni_R
= 0.0421 x 290.801 = 12.2427g

From the chemical equation, *0.5 mol of* $Zn(NO_3)_2.6H_2O$ *is* needed to produce 1 mol of *NZFE*

= $\frac{0.5\ mol}{1\ mol\ of\ NZFE}$ x 0.0841 mol of *NZFE*

= 0.0421 mol

m Fe_R = n Fe_R x MW Fe_R
= 0.0421 x 297.5166 = 12.5254g

From the chemical equation, *2 mol of* $Fe(NO_3)_3.9H_2O$ is needed to produce 1 mol of *NZFE*

= $\frac{2\ mol}{1\ mol\ of\ NZFE}$ x 0.0847 mol of *NZFE*

= 0.1682 mol

m Fe_R = n Fe_R x MW Fe_R
= 0.1682 x 404.0388 = 67.9593g

x = 0.75

$Ni_{1-x}\,Zn_x\,Fe_2\,O_4 \rightarrow Ni_{0.25}\,Zn_{0.75}\,Fe_2O_4$

Chemical equation:

$0.255Ni\,(NO_3)_2.6H_2O + 0.75Zn\,(NO_3)_2.6H_2O + 2Fe\,(NO_3)_3\,.9H_2O \rightarrow$

$Ni_{05}\,Zn_{0.5}\,Fe_2O_4 + volatiles$

Sample targeted mass = 20g

No. of moles NZFE = $\frac{m}{MW} = \frac{20g}{0.25[58.6934]+0.75[65.409]+2[55.845]+4[15.9999]}$

= 0.0836 mol

From the chemical equation, *0.25mol of* $Ni\,(NO_3)_2.6H_2O$ is needed to produce 1 mol of *NZFE*

n $Ni_R = \frac{0.25\,mol}{1\,mol\,NZFE}$ x 0.0836 mol of *NZFE*

= 0.0209 mol

m Ni_R = n Ni_R x MW Ni_R

= 0.0209 x 290.801 = 6.0777g

From the chemical equation, *0.75 mol of* $Zn\,(NO_3)_2.6H_2O$ *is* needed to produce 1 mol of *NZFE*

= $\frac{0.75\,mol}{1\,mol\,of\,NZFE}$ x 0.0836 mol of *NZFE*

= 0.0627 mol

m Fe_R = n Fe_R x MW Fe_R

= 0.0627 x 297.5166 = 18.6543g

From the chemical equation, *2mol of* $Fe\,(NO_3)_3\,.9H_2O$ is needed to produce 1 mol of *NZFE*

= $\frac{2\,mol}{1\,mol\,of\,NZFE}$ x 0.0836 mol of *NZFE*

= 0.1672 mol

m Fe_R = n Fe_R x MW Fe_R

= 0.1672 x 404.0388 = 67.5553g

x = 1

$Ni_{1-x}\, Zn_x\, Fe_2\, O_4$ $\rightarrow$ *$Zn\,Fe_2O_4$*

Chemical equation:

$$Zn\,(NO_3)_2.6H_2O + 2Fe\,(NO_3)_3\,.9H_2O \rightarrow Zn\,Fe_2O_4 + volatiles$$

Sample targeted mass = 20g

No. of moles NZFE = $\frac{m}{MW}$ = $\frac{20g}{[65.409]+2[55.845]+4[15.9999]}$

= 0.0831 mol

From the chemical equation, *1 mol of $Zn\,(NO_3)_2.6H_2O$ is* needed to produce 1 mol of *NZFE*

= $\frac{1\ mol}{1\,mol\ of\ NZFE}$ x 0.0831 mol of *NZFE*

= 0.0831 mol

m Fe_R = n Fe_R x MW Fe_R
= 0.0831 x 297.5166 = <u>24.7236g</u>

From the chemical equation, *$2Fe\,(NO_3)_3\,.9H_2O$* is needed to produce 1 mol of *NZFE*

= $\frac{2\,mol}{1\,mol\ of\ NZFE}$ x 0.0831 mol of *NZFE*

= 0.1662 mol

m Fe_R = n Fe_R x MW Fe_R
= 0.1662 x 404.0388 = <u>67.1512g</u>